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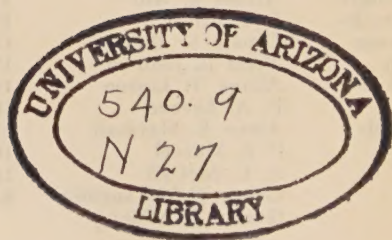Louis E. Wise
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FOREWORD

The arrangement of Volume 3 of the Annual Survey of American Chemistry is similar to that of the first two volumes. The Editorial Board has adopted the policy of varying the subjects treated from year to year, which will mean that certain less active fields will be covered only every second or third year. Different authors also will be asked to write the reviews, thus distributing the effort of preparing the chapters among the authorities in the fields involved, and giving the readers more than one man's point of view on a particular subject.

The publication of the first volume of the Survey was an experiment, and its appearance caused considerable comment as to the desirability of such a review. While there is still some opposition to the policy of publishing a Survey entirely national in character, the support that the first two volumes have received indicates that it fills a useful place in technical literature.

The Division of Chemistry and Chemical Technology takes this opportunity of thanking the many contributors to Volume 3 who have made the publication possible. It also wishes to thank Dr. C. J. West, the Editor, who has given freely of his experience, as well as his time, in welding the individual reports into an effective volume, and Miss Callie Hull, of the Research Information Service, who has verified all the literature citations and compiled the author index.

FRANK C. WHITMORE.

Washington, D. C.
September 10, 1928

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Chapter I.

Physical Chemistry of Electrolytic Solutions.

Herbert S. Harned,

Professor of Chemistry, Yale University

It is safe to say that no theoretical investigation of general significance dealing with the nature of electrolytic solutions has appeared during the last year. A number of excellent experimental contributions have been made and some investigations which deal with special phases of the theory are well worth careful consideration.

Conductance of Electrolytic Solutions. An extraordinarily extensive and careful study of the methods of measurement of the conductances of electrolytic solutions has been made by Jones and Josephs.[1] The sources of errors in such determinations have been analyzed and to a large extent eliminated. Among the many improvements may be mentioned a new method of grounding the bridge and a new design of a resistance box suitable for this type of measurement. As a final result, they have constructed a bridge which can be used with either direct or alternating current and which has an extraordinary sensitivity.

Transference Numbers. MacInnes, Cowperthwaite, and Huang[2] have continued their work on the improvement of measurement of transference numbers by the method of the moving boundary. Under favorable conditions, they show from their data with silver nitrate solutions that the adjustment of their apparatus can be made to within 0.02%.

Electrodes. Gerke and Geddes[3] have described a new hydrogen electrode vessel and have determined the potential of the $0.1M$ mercury-mercurous bromide-bromide ion electrode. Randall and Young[4] have shown that the presence of dissolved air

[1] Jones and Josephs, *J. Am. Chem. Soc.*, **50**: 1049 (1928).
[2] MacInnes, Cowperthwaite, and Huang, *J. Am. Chem. Soc.*, **49**: 1710 (1927).
[3] Gerke and Geddes, *J. Phys. Chem.*, **31**: 886 (1927).
[4] Randall and Young, *J. Am. Chem. Soc.*, **50**: 989 (1928).

in the calomel electrode containing hydrochloric acid may cause an error of from 1 to 3 mv. They have also recalculated the potentials of the molal and the deci-molal calomel, the molal silver chloride, and the molal chlorine electrodes. Nielsen and Brown [5] have studied the two phase copper amalgam-cuprous chloride electrode.

Measurements of Activity Coefficient. An unusually accurate series of electromotive force measurements in dilute solutions of zinc sulfate has been obtained by Bray [6] from the cells:

$Zn-Hg(2 \text{ phase}) \mid ZnSO_4(m) \mid PbSO_4(s) \mid Pb-Hg(2 \text{ phase})$.

The results were found to be in excellent agreement with the limiting equation of the theory of Debye and Hückel. Getman [7] has determined the activity coefficients of cadmium chloride, bromide, iodide and sulfate in aqueous solutions from electromotive force measurements. Nielsen and Brown [8] in a similar manner have measured the activity coefficients of copper sulfate.

Freezing point measurements of solutions of hydrochloric acid of strengths from 0.1 to 1 molal have been made by Chadwell,[9] who found that the activity coefficient of the acid calculated therefrom agreed very well with that obtained from electromotive force measurements. Randall and Young [4] have recalculated the activity coefficient of hydrochloric acid from electromotive force and freezing point data.

The vapor pressures of saturated aqueous solutions of potassium and sodium chlorides and sulfates have been determined through the temperature range of from 20° to 50° by Leopold and Johnston.[10] From these and other data, a careful investigation has been made of the relative vapor pressure lowerings of some of these solutions.

Cohn, Heyroth, and Menkin [11] have made an extensive study of acetic acid-sodium acetate mixtures by means of the hydrogen electrode. This very thorough work adds considerably to the accurate knowledge of the pH of buffer solutions. Hall and Conant [12, 13] have employed the chloranil electrode in glacial acetic acid solutions. They were thus able to obtain electrometric titra-

[5] Nielsen and Brown, *J. Am. Chem. Soc.*, **50**: 9 (1928).
[6] Bray, *J. Am. Chem. Soc.*, **49**: 2372 (1927).
[7] Getman, *J. Phys. Chem.*, **32**: 91, 940 (1928).
[8] Nielsen and Brown, *J. Am. Chem. Soc.*, **49**: 2423 (1927).
[9] Chadwell, *J. Am. Chem. Soc.*, **49**: 2795 (1927).
[10] Leopold and Johnston, *J. Am. Chem. Soc.*, **49**: 1974 (1927).
[11] Cohn, Heyroth and Menkin, *J. Am. Chem. Soc.*, **50**: 696 (1928).
[12] Hall and Conant, *J. Am. Chem. Soc.*, **49**: 3047 (1927).
[13] Conant and Hall, *J. Am. Chem. Soc.*, **49**: 3062 (1927).

tion curves of many organic bases which could not be titrated in aqueous solution. From these data, the relative strengths of a large number of bases were roughly estimated.

By means of measurements of the partition coefficients of some organic acids between aqueous salt solutions and normal dibutyl ether, Randall and Failey [14] have determined their activity coefficients in the aqueous solutions.

The activity coefficients of sodium silicate have been studied by Randall and Cann.[15] They find that sodium metasilicate behaves as a typical unibivalent electrolyte. The low activity coefficients of the acid silicates are thought to be caused by the formation of ionic micelles.

The activity coefficients of lead bromide in a number of aqueous salt solutions have been determined from solubility determinations by Randall and Vietti.[16] Randall and Chang [17] have measured the solubility of thallous chloride in magnesium sulfate and lanthanum nitrate solutions.

Liquid Junction Potentials. An important contribution to the theory of liquid junction potentials has been made by Taylor.[18] He has shown that the measurements of the electromotive forces of cells with transference can yield no information concerning ionic free energies. This consideration makes the liquid junction depend on a purely arbitrary definition of individual ion activity coefficients as pointed out from somewhat different considerations by Harned.[19] This means that no measurement of homogeneous ionic solutions can give values of the ionic free energies and that ionic activity coefficients or ionic activities will only be serviceable in certain numerical calculations. The problems of homogeneous ionic solutions should always be approached by the use of activity coefficient products or their ratios. Taylor has also deduced, by an exact method, the differential equation for the interdiffusion of electrolytes and has extended Henderson's equation for liquid junction potentials in such a way as to take into account variable ionic mobilities and activity coefficients. This equation is an approximation.

Roberts and Fenwick [20] have shown that a reproducible liquid

[14] Randall and Failey, *J. Am. Chem. Soc.*, **49**: 2678 (1927).
[15] Randall and Cann, *J. Am. Chem. Soc.*, **50**: 347 (1928).
[16] Randall and Vietti, *J. Am. Chem. Soc.*, **50**: 1526 (1928).
[17] Randall and Chang, *J. Am. Chem. Soc.*, **50**: 1535 (1928).
[18] Taylor, *J. Phys. Chem.*, **31**: 1478 (1927).
[19] Harned, *J. Phys. Chem.*, **30**: 433 (1926).
[20] Roberts and Fenwick, *J. Am. Chem. Soc.*, **49**: 2678 (1927).

junction potential may be obtained by causing the two solutions in question to flow on each side of a sheet of mica which has been perforated with a small hole.

Specific Heats of Salt Solutions. An adiabatic twin calorimeter for the determination of the specific heats of salt solutions has been developed by Gucker,[21] and the specific heats of solutions of potassium chloride and nitrate have been determined. The apparatus shows marked improvement over that previously employed by Richards and Gucker.[22]

Homogeneous Catalysis. Kilpatrick[23] has made an interesting study of a reaction of the type $A^\circ + B^{+++} \rightarrow (A,B)^{+++} \rightarrow$ products. He finds that as the ionic strength is increased by the addition of potassium nitrate, the velocity constant remains nearly constant. The result is contrary to the activity rate theory and is interpreted as giving support to the theory of Brönsted.

Terry[24] has found that the observed reaction velocity coefficient, K_{obs}, of hydrolysis of ethyl acetate catalyzed by hydrochloric acid may be approximately expressed by the equation

$$K_{obs} \left(\frac{\gamma_{KOH}}{\gamma'_{HCl}} \right) = K'_o d$$

where γ_{KOH}, γ'_{HCl}, are the activity coefficients of potassium hydroxide and hydrochloric acid in the aqueous solutions, K_{obs}, the reaction velocity constant divided by the catalyst concentration, and $K'_o d$ turns out to be a constant. This equation has also been applied to the catalysis of the ester in potassium and sodium chloride solutions. The reciprocal relation

$$K_{obs} \left(\frac{\gamma'_{HCl}}{\gamma_{KOH}} \right) = K_o d$$

has also been found to be approximately valid in the case of hydroxyl ion catalysis. Terry and Stieglitz[25] have improved the method of measuring the velocity of saponification of esters. Wilson and Terry[26] have investigated the velocity of saponification of ethyl acetate by sodium hydroxide in sodium chloride, acetate and nitrate solutions.

Åkerlöf[27] has continued his investigation of the hydroxyl ion

[21] Gucker, *J. Am. Chem. Soc.*, **50**: 1005 (1928).
[22] Richards and Gucker, *J. Am. Chem. Soc.*, **47**: 1876 (1925).
[23] Kilpatrick, *J. Am. Chem. Soc.*, **50**: 358 (1928).
[24] Terry, *J. Am. Chem. Soc.*, **50**: 1239 (1928).
[25] Terry and Stieglitz, *J. Am. Chem. Soc.*, **49**: 2216 (1927).
[26] Wilson and Terry, *J. Am. Chem. Soc.*, **50**: 1250 (1928).
[27] Akerlöf, *J. Am. Chem. Soc.*, **49**: 2955 (1927).

catalysis of decomposition of diacetone alcohol in aqueous solutions. He finds that in the strong solutions of potassium, sodium and lithium hydroxides the velocity is given by

$$v = k m_{\text{MOH}} \sqrt{\gamma_M \gamma_{\text{OH}}},$$

where m_{MOH} is the concentration of the hydroxide and $\sqrt{\gamma_M \gamma_{\text{OH}}}$ its activity coefficient. This relation does not hold in the salt solutions. He does find, however, that in hydroxide-salt mixtures at constant total molality

$$\log \frac{k}{m_{\text{MOH}}} = \alpha\, m_{\text{MOH}} + \text{constant},$$

where α is a constant. Thus, the logarithm of the velocity constant-catalyzing hydroxide ratio varies linearly with the hydroxide concentration at constant total molality.

Åkerlöf [28] has also studied the catalysis of this reaction by weak organic bases in salt solutions. Further,[29] he has investigated this decomposition catalyzed by sodium hydroxide in various solvents such as water-methyl alcohol, methyl-n-propyl alcohol mixtures, etc.

Harned and Hawkins [30] have investigated the catalysis of certain esters by mono- and di-chloroacetic acids in halide and sulfate solutions. They have shown how the ionic activity products of these acids in the salt solutions may be computed from the kinetic data.

A careful investigation of the iodide ion catalysis of hydrogen peroxide in neutral salt solutions has been carried out by French.[31] He also investigated the hydroxyl ion catalysis of nitrosotriacetone-amine in certain halide solutions. Kautz and Robinson [32] have measured the inversion of cane sugar by hydrochloric acid in the presence of neutral salts.

[28] Akerlöf, *J. Am. Chem. Soc.*, **50**: 733 (1928).
[29] Akerlöf, *J. Am. Chem. Soc.*, **50**: 1272 (1928).
[30] Harned and Hawkins, *J. Am. Chem. Soc.*, **50**: 85 (1928).
[31] French, *J. Phys. Chem.*, **32**: 401 (1928).
[32] Kautz and Robinson, *J. Am. Chem. Soc.*, **50**: 1022 (1928).

Chapter II.

Phase Equilibrium Data.

Arthur E. Hill,

Professor of Chemistry, New York University

Limiting the following survey to those studies in heterogeneous equilibrium which are not commonly treated under other headings because of their relationship to accepted classes of chemical theory, we find that the output of the past twelve months from American laboratories has not been notably different in amount or kind from that of the preceding year. The forty-five publications will be classified according to the number of components in the systems studied.

One-Component Systems. Vapor pressure measurements have been made in the case of several liquids; the vapor pressure of germanium tetrachloride [1] has been measured from 4 to 186° C., that of methylene chloride [2] from 186.1 to 311.5° abs., and the pressures of isopropyl and of *tert*.-butyl alcohols [3] up to 90° C., all by static methods. The vapor pressure of pure sulfur dioxide [4] has also been measured, in connection with work on its aqueous solutions. The densities of liquid and of gaseous carbon dioxide [5] have been measured by the method of relative volumes from − 5.8 to 22.9° C.; the presence of water does not affect the density enough to be detected in the experimental method used, and its solubility in the liquid phase is calculated as less than 0.05%. Qualitative evidence of a hydrate at about 4° C. was found.

Two-Component Systems. The vapor pressures of several aqueous solutions have been determined. The system sulfur dioxide-water [4] has been thoroughly investigated and measurements made not only of aqueous solutions of various concentra-

[1] Brewer and Dennis, *J. Phys. Chem.*, **31**: 1101 (1927).
[2] Perry, *J. Phys. Chem.*, **31**: 1737 (1927).
[3] Parks and Barton, *J. Am. Chem. Soc.*, **50**: 24 (1928).
[4] Maass and Maass, *J. Am. Chem. Soc.*, **50**: 1352 (1928).
[5] Lowry and Erickson, *J. Am. Chem. Soc.*, **49**: 2729 (1927).

tions over a limited temperature range but also of the two-liquid system as well. Vapor pressures of saturated solutions of potassium chloride, potassium sulfate, potassium bichromate, sodium chloride and sodium sulfate [6] have been carefully measured and the technique of such experiments improved. The vapor pressures of amalgams of potassium,[7] sodium and caesium [8] have been made; the deviations from Raoult's law are naturally very great. Of hydrated salts, calcium nitrate [9] in the form of its several hydrates appears to be the only one subjected to vapor tension measurements but the data are of exceptional completeness. The single publication dealing entirely with general considerations in the field of heterogeneous equilibrium is on the equilibrium pressure of coexisting salt hydrates below $0°$ [10]; from the relation $\log p = \dfrac{Q}{2.3\,RT} + B$ for the systems $S + S_2 + V$ and $Ice + V$, it is shown the slope of the two curves, for all cases in which thermal data are reliable, is such that the curves cannot meet below $0°$, and that an invariant point representing two solid hydrates, ice and vapor, is therefore non-existent.

In the field of condensed systems, measurements have been fairly numerous. With aqueous solutions as the liquid phase, solubilities of the following salts have been determined: lithium perchlorate,[11] which yields a trihydrate and a monohydrate with congruent melting points; calcium nitrate,[12] which has been studied with respect to both stable and metastable hydrates and which, with the previously mentioned work [9] on vapor pressures, gives us one of the very few completely studied systems for a hydrated salt and water; magnesium sulfate,[13] which has been studied from 68 to $240°$ C. by means of well devised apparatus; and barium n-butyrate,[14] in which case the solubility has a minimum at about $30°$ C. The ice curve for hydrogen chloride in water [15] has been determined up to 1.03 molal concentration. The solubility of m-nitroaniline in water from 0 to $34°$ has been measured [16] and much needed data on the solubility and fixed temperature points

[6] Leopold and Johnston, *J. Am. Chem. Soc.*, **49**: 1974 (1927).
[7] Millar, *J. Am. Chem. Soc.*, **49**: 3003 (1927).
[8] Bent and Hildebrand, *J. Am. Chem. Soc.*, **49**: 3011 (1927).
[9] Ewing, *J. Am. Chem. Soc.*, **49**: 1963 (1927).
[10] Austin, *J. Am. Chem. Soc.*, **50**: 333 (1927).
[11] Simmons and Ropp, *J. Am. Chem. Soc.*, **50**: 1650 (1928).
[12] Ewing, Krey, Law and Lang, *J. Am. Chem. Soc.*, **49**: 1958 (1927).
[13] Robson, *J. Am. Chem. Soc.*, **49**: 2772 (1927).
[14] Wing, *J. Am. Chem. Soc.*, **49**: 2859 (1927).
[15] Chadwell, *J. Am. Chem. Soc.*, **49**: 2795 (1927).
[16] Walton and Finzel, *J. Am. Chem. Soc.*, **50**: 1508 (1928).

for phenol and water [17] have been supplied, fixing the diagram with respect to the little known stable hydrate as well as the better known metastable anhydrous form.

Several non-aqueous two-component systems have been studied. With liquid ammonia as solvent, the solubility of non-radiated chlolesterol has been measured from -38 to $48°$ C.[18] Liquid carbon dioxide has been shown, by means of its solvent action upon iodine and upon naphthalene,[19] to have an internal pressure much less than those liquids commonly used as solvents. Investigation of the thirty solubility curves in the fifteen possible binary mixtures of the dinitrobenzenes and nitroanilines [20] show that the curve is in all cases not far from the ideal calculated from the heat of fusion. There is no appreciable formation of solid solution even between those three pairs in which the relative position of the substituents is the same. On the other hand, the three like pairs of chloronitrobenzenes and of bromonitrobenzenes [20] form a complete series of solid solutions, and p-toluic acid and p-chlorobenzoic acid [20] show limited mutual solubility. Acetanilide and propionanilide [21] form a $1:1$ compound. Using equiatomic quantities of sodium, potassium, and iodine at $700°$ C.,[22] the equilibrium between the liquid salt phase and the liquid alloy phase has been studied. The solubility of silver in mercury [23] has been measured up to $200°$ C., using a new type of solubility tube. The results of a thermochemical study of the system cadmium-mercury [24] show that special conditions must be observed in order to obtain true equilibration in the solid amalgams. The method of electrical conductivity has been used on cold-worked alloys of lead and antimony [25] in order to determine the limits of solubility in the solid phase.

Multi-Component Systems. A number of three-component systems have been studied in which water is the solvent. Leading to a calculation of the activity of moderately insoluble salts, measurements have been made of the solubility of lead bromide [26] in aqueous solutions containing lead nitrate, barium nitrate, cad-

[17] Jones, *J. Phys. Chem.*, **31**: 1316 (1927).
[18] Gustavson and Goodman, *J. Am. Chem. Soc.*, **49**: 2526 (1927).
[19] Quinn, *J. Am. Chem. Soc.*, **50**: 672 (1928).
[20] Johnston and Jones, *J. Phys. Chem.*, **32**: 593 (1928).
[21] Gilbert and Clarke, *J. Am. Chem. Soc.*, **49**: 2296 (1927).
[22] Sill, *J. Phys. Chem.*, **32**: 466 (1928).
[23] Sunier and Hess, *J. Am. Chem. Soc.*, **50**: 662 (1928).
[24] Richards, Frevert and Teeter, Jr., *J. Am. Chem. Soc.*, **50**: 1293 (1928).
[25] Schumacher and Bouton, *J. Am. Chem. Soc.*, **49**: 1667 (1927).
[26] Randall and Vietti, *J. Am. Chem. Soc.*, **50**: 1526 (1928).

mium bromide and potassium bromide; of thallous chloride [27] in the presence of magnesium sulfate and of lanthanum nitrate; and of lead monoxide (both red and yellow forms) and of basic lead carbonate [28] in alkaline solutions. Isotherms at 15, 25 and 30° C. show the limits of the two-liquid systems formed from methyl benzoate, methanol and water.[29] In the sodium carbonate-bicarbonate-water system,[30] the double salt Trona is found to be stable from 21.26° C. upward, in contact with solutions of increasing range of salt content. A study of the system sodium carbonate-potassium carbonate-water at 40° C.[31] indicates the existence of a trihydrate of sodium carbonate stable above that temperature, which would make the existing solubility data on sodium carbonate refer to the metastable monohydrate. The system water and the sulfates of sodium and magnesium [32] have been thoroughly studied up to 210°, with correction and amplification of earlier data on solubility and on invariant points.

Solubilities of paraffin waxes have been the topic of three investigations, with pure hydrocarbons [33] as solvent in one case and petroleum oils [34] in the second; in the third solid solution has been indicated as the condition in the solid phase for the paraffin waxes,[35] as determined by freezing-point curves and by cooling curves. The solubility of nitrocellulose in mixtures of various organic solvents has also been measured.[36]

Only a single study on equilibrium in solid phases of a multi-component system has been noted, but it contains further data on a system of obvious importance — calcium oxide, aluminum oxide and ferric oxide.[37] For the various systems containing ferrous and ferric oxide, aluminum oxide and silica,[38] a study of the regions of complete and of incomplete solubility in the liquid state, at high temperatures, has been made. A study of glasses made by under-cooling n-propyl alcohol and propylene glycol [39] shows a temperature at or near which a rapid change of properties occurs, for which phenomenon various explanations are offered.

[27] Randall and Chang, *J. Am. Chem. Soc.,* **50**: 1535 (1928).
[28] Randall and Spencer, *J. Am. Chem. Soc.,* **50**: 1572 (1928).
[29] Gilbert and Lauer, *J. Phys. Chem.,* **31**: 1050 (1927).
[30] Hill and Bacon, *J. Am. Chem. Soc.* **49**: 2487 (1927).
[31] Bain, *J. Am. Chem. Soc.,* **49**: 2734 (1927).
[32] Blasdale and Robson, *J. Am. Chem. Soc.,* **50**: 35 (1928).
[33] Weber and Dunlap, *Ind. Eng. Chem.,* **20**: 383 (1928).
[34] Sullivan, McGill and French, *Ind. Eng. Chem.,* **19**: 1042 (1927).
[35] Meyers and Stegeman, *Ind. Eng. Chem.,* **20**: 638 (1928).
[36] Reid and Hofmann. *Ind. Eng. Chem.,* **20**: 497 (1928).
[37] Hansen, Brownmiller and Bogue, *J. Am. Chem. Soc.,* **50**: 396 (1928); Hansen and Brownmiller, *Am. J. Sci.,* **15**: 225 (1928).
[38] Greig, *Am. J. Sci.,* **14**: 473 (1927).
[39] Parks and Huffman, *J. Phys. Chem.,* **31**: 1842 (1927).

Several equilibria between solids and gas have been studied : they include an investigation of the reaction of tin [40] with water vapor and with carbon dioxide, from which an indirect calculation of the water-gas equilibrium can be made, and studies of the reduction of thorium oxide[41] and of aluminum oxide [42] by carbon. New thermal data have also been furnished by use of which the equilibrium constants may be computed for the reactions involved in the reduction of ferric oxide.[43]

Of interest in the determination of solubilities is a new device, called an equilibrator,[44] which by rotation acts as an automatic circulating pump, forcing a gas or vapor to bubble continuously and in turn through two separated liquids.

[40] Eastman and Robinson, *J. Am. Chem. Soc.*, **50**: 1106 (1928).
[41] Prescott and Hincke, *J. Am. Chem. Soc.*, **49**: 2744 (1927).
[42] Prescott and Hincke, *J. Am. Chem. Soc.*, **49**: 2753 (1927).
[43] Furnas and Brown, *Ind. Eng. Chem.*, **20**: 507 (1928).
[44] Jones and Kaplan, *J. Am. Chem. Soc.*, **50**: 1600 (1928).

Chapter III.

Kinetics of Homogeneous Gas Reactions.

F. O. Rice,

Johns Hopkins University

The past few years have seen a very great extension of the interest shown in homogeneous gas reactions, particularly in connection with first order reactions. Not only have some of the more well known reactions been examined critically but several new unimolecular reactions have been discovered and some of them investigated very completely. We have therefore available a number of homogeneous gas reactions whose mechanism is established beyond any doubt. It is encouraging to find that the theoretical development in this field is proceeding apace, since about a dozen purely theoretical papers have appeared in the last two years. A monograph [1] on statistical mechanics is now available containing several chapters dealing with reaction rates.

Nitrogen Pentoxide. Fazel and Karrer [2] point out that the decomposition of nitrogen pentoxide by blue light (4600-4000 λ) is an example of a photosensitized reaction, the energy absorbed by the nitrogen dioxide molecules from the light being transferred to nitrogen pentoxide molecules by means of collisions of the second kind. Nitrogen pentoxide, free from nitrogen peroxide or protected by a screen of the peroxide, is not decomposed by the blue light. Busse and Daniels, [3] however, think that the hypothesis of Norrish [4] is correct; he postulates that nitrogen peroxide under the influence of light gives nitric oxide and oxygen and that the nitric oxide and nitrogen pentoxide then react. In support of this view Busse and Daniels show that nitric oxide is immediately oxidized in presence of nitrogen pentoxide and that bromine

[1] Tolman, "Statistical Mechanics." New York, Chem. Cat. Co., 1927. 334 p.
[2] Fazel and Karrer, *J. Am. Chem. Soc.*, **48**: 2837 (1926).
[3] Busse and Daniels, *J. Am. Chem. Soc.*, **49**: 1257 (1927).
[4] Norrish, *Nature*, **119**: 123 (1927).

vapor, whose absorption spectrum is similar to that of nitrogen dioxide, does not act as a photosensitiser. The paper also contains a number of interesting results on the effect of foreign gases. The thermal decomposition rate of nitrogen pentoxide is not affected by collisions with bromine, chlorine, carbon monoxide or hydrogen. Dickinson and Baxter [5] also agree that gaseous nitrogen dioxide is decomposed photochemically into nitric oxide and oxygen and in addition measured the quantum yield of the reaction.

Rice and Getz [6] examined the decomposition of nitrogen pentoxide from the point of view that it might be a heterogeneous reaction taking place on dust particles. No evidence of any heterogeneity was obtained, the dust-free gas decomposing at the normal rate. Nitrogen pentoxide prepared from silver nitrate and chlorine also decomposed at the normal rate. Lueck's [7] results for the decomposition in solution in carbon tetrachloride were confirmed; in addition it was found that nitrogen pentoxide decomposed at less than one tenth of the normal rate when dissolved in 100% nitric acid.

Hibben [8, 9] has studied the decomposition of nitrogen pentoxide over a pressure range of 0.18-0.0018 mm. Hg. He finds, in contradiction to the results of Hirst and Rideal,[10] that the rate remains constant even down to the lowest pressure investigated. It would seem somewhat premature, therefore, to discuss the low pressure measurements until further work has been done, preferably using a different method of measurement.

Azomethane. The work of Ramsperger [11, 15] has given us another example of a unimolecular reaction which is now being studied with great completeness. Azomethane decomposes at a measurable rate in the neighborhood of 900° C. and is practically free from wall effects or simultaneous reactions. The heat of activation is 51,200 cal. It is homogeneous at all pressures but below 4 cm. initial pressure the rate falls off with diminishing pressure.[12] This is in marked contrast to the decomposition of azoisopropane whose rate of decomposition is constant even to pressures of 0.025 cm.[13]

[5] Dickinson and Baxter, *J. Am. Chem. Soc.*, **50**: 774 (1928).
[6] Rice and Getz, *J. Phys. Chem.*, **31**: 1572 (1927).
[7] Lueck, *J. Am. Chem. Soc.*, **44**: 757 (1922).
[8] Hibben, *Proc. Nat. Acad. Sci.*, **13**: 626 (1927).
[9] Hibben, *J. Am. Chem. Soc.*, **50**: 940 (1928).
[10] Hirst and Rideal, *Proc. Roy. Soc.*, **109A**: 526 (1925).
[11] Ramsperger, *J. Am. Chem. Soc.*, **49**: 912 (1927).
[12] Ramsperger, *J. Am. Chem. Soc.*, **49**: 1495 (1927).
[13] Ramsperger, *J. Am. Chem. Soc.*, **50**: 714 (1928).

Azomethane shows continuous absorption [14] in the ultraviolet between 4000 and 2900 Å and when decomposed by light of 3666 Å it gives two molecules decomposed per quantum absorbed. The quantum yield is independent of the pressure between 0.1 and 25 cm. This work makes unlikely any explanation for the thermal decomposition based on a chain mechanism.

Pinene. The decomposition of pinene [16] has proved to be a homogeneous first order reaction having approximately the same reaction rate whether as a gas, a pure liquid or in solution in petrolatum, acetophenone or α-methylnaphthalene. Since the concentration of pinene in these experiments was varied over 100-fold from the gas to the pure liquid reactions, there is reasonable certainty that we have a true first order reaction. The reaction occurs at a measureable rate in the neighborhood of 200° C. and has a heat of activation of 43,700 cal.

Radiation Hypothesis. Daniels [17] has given a very useful review of this hypothesis and concludes that "at present the evidence seems to indicate that radiation is not important in ordinary thermal reaction." Hibben [18] has studied the effect of infra-red radiation on the decomposition of ozone and nitrous oxide, his work providing two more examples of gas reactions that are unaffected by infra-red radiation. Mayer [19] measured the absorption coefficient of nitrogen pentoxide for the radiation emitted from a black body at 100 and 202° C., using an apparatus in which there were no windows between the source of radiation and the thermopile. The measurements showed that the absorption coefficient under these conditions were of the same order of magnitude as for wavelengths shorter than 7μ. This is an important experiment because it disposes of the modified form of the radiation hypothesis which postulates that activation occurs by successive absorption of quanta of low frequency. This would require very intense absorption bands at wavelengths longer than 7μ and none exist.

Finally there is the molecular beam experiments of Lewis and Mayer [20] and Mayer.[19] A beam of pinene molecules was allowed to pass through a cylindrical platinum furnace, the whole apparatus being highly evacuated, so that the number of collisions of

[14] Ramsperger, *J. Am. Chem. Soc.*, **50**: 123 (1928).
[15] Ramsperger, *Proc. Nat. Acad. Sci.*, **13**: 849 (1927).
[16] Smith, *J. Am. Chem. Soc.*, **49**: 43 (1927).
[17] Daniels, *Chem. Reviews*, **5**: 39 (1928).
[18] Hibben, *J. Am. Chem. Soc.*, **50**: 937 (1928).
[19] Mayer, *J. Am. Chem. Soc.*, **49**: 3033 (1927).
[20] Lewis and Mayer, *Proc. Nat. Acad. Sci.*, **13**: 623 (1926).

molecules in the beam was negligibly small. The furnace was heated to various temperatures, in some cases such that only the 10^{-6} part of the pinene should have remained unracemised. No racemisation was observed in any experiment, so that we may conclude that any form of radiation hypothesis alone cannot account for chemical reaction rates.

Theoretical. Since it has now been amply demonstrated that the radiation hypothesis can no longer be regarded as an explanation of molecular reactions we are forced to consider a collision mechanism as the basis for the production of activated molecules in unimolecular processes. The production of activated molecules is, therefore, mainly a bimolecular process which is supposed to be very rapid as compared to the decomposition of the activated molecules; this is a true unimolecular process, being independent of collisions with other molecules or with the walls. The large number of theoretical papers that have appeared [21] consider in detail this mechanism and make comparisons of theoretical calculations with experimental results.

It has usually been supposed that the energy of activation is confined to the comparatively few degrees of freedom associated with energy of translation and rotation. Calculations made on this basis show that molecules cannot be activated fast enough to account for any of the known unimolecular reactions. If, however, we assume that molecules can exchange internal energy at collision [22] it is possible to obtain greatly increased rate of activation. It is along these lines that most of the theoretical workers have attempted to explain unimolecular reactions. Fowler and Rideal assumed that when two molecules collided the total internal energy and the relative kinetic energy could flow into one molecule and if this total was equal to or greater than the energy of activation, an activated molecule was produced. There are two difficulties associated with this assumption which have been discussed by Tolman, Yost and Dickinson [23] and by Lewis.[24] In most of the activating collisions the total energy available will be only slightly greater than the energy of activation so that all the energy would have to flow into one molecule; this seems a rather extreme assumption. The second difficulty is connected with the very large

[21] In addition to references cited, *cf.* Waldauer and Patton, *J. Phys. Chem.* **31**: 1433 (1927); Lewis, *Proc. Nat. Acad. Sci.*, **13**: 546 (1927).
[22] Hinshelwood, *Proc. Roy. Soc.*, 113A: 230 (1927); Fowler and Rideal, *Proc. Roy. Soc.*, 113A: 570 (1927).
[23] Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, **13**: 188 (1927).
[24] Lewis, *Science*, **66**: 331 (1927).

deactivational diameters. From the principle of microscopic reversibility the number of activating collisions must be equal to the number of deactivating collisions; calculations based on this and using the measured rate of decomposition of nitrogen pentoxide give surprisingly large areas for the deactivational collisions; even using Lewis' amended calculations, these are one to two orders too high. Lewis quotes a number of examples in which excited atoms have very large effective diameters but nevertheless it seems difficult to imagine nitrogen pentoxide with its very low energy of excitation possessing such a large diameter.

Rice and Ramsperger [25] have developed expressions for reaction rate which show satisfactory agreement with the observed falling off in rate at low pressures. The work is based on the use of a collision hypothesis and classical statistical mechanics with some modifications suggested by quantum theory. It is clear that if our process of activation is dependent on collision, its rate will diminish at low pressures so that finally at low enough pressures the reaction rate will be affected. These authors consider two theories: In theory 1 it is assumed that "an activated molecule has a certain chance of reacting, independent of the distribution of energy among the degrees of freedom and independent of the amount it has above that necessary for activation." They conclude that this theory does not explain the falling off of direction rate with pressure. In theory 2 it is assumed that "a particular degree of freedom should have a minimum energy, say ε_o, but that it is able to obtain this energy, even between collisions, from other parts of the molecule." By making use of only a few degrees of freedom of a molecule, the authors find very satisfactory agreement between the calculated falling off and the observed falling off of reaction rate at low pressures. This work has been continued by Rice [26, 27] by introducing modifications called for, if the motions of the molecule be considered quantized. Kassel [28, 29] has developed a very similar theory to Theory 2 of Rice and Ramsperger, except that he assumes that the energy ε_o must be localized in two squared terms or in one degree of freedom in the classical sense. A very interesting general paper by Kassel [30] on the region of existence of unimolecular reactions suggests that a

[25] Rice and Ramsperger, *J. Am. Chem. Soc.*, **49**: 1617 (1927); **50**: 617 (1928).
[26] Rice, *Proc. Nat. Acad. Sci.*, **14**: 113 (1928).
[27] Rice, *Proc. Nat. Acad. Sci.*, **14**: 118 (1928).
[28] Kassel, *J. Phys. Chem.*, **32**: 225 (1928).
[29] Kassel, *Proc. Nat. Acad. Sci.*, **14**: 23 (1928).
[30] Kassel, *J. Am. Chem. Soc.*, **50**: 1344 (1928).

typical unimolecular gaseous decomposition passes through three stages : the first stage is a bimolecular reaction occurring mainly at collision ; the second stage is a unimolecular reaction in which the activated molecules spontaneously decompose ; the third stage is again a bimolecular reaction and represents the rate of production of active molecules at low pressures.

There is the possibility that the energy of translation of gas molecules may not be transferred readily at collision to the internal degrees of freedom, where it is available for activation. This has been tested [31] by considering the absorption of high frequency sound waves in gases ; a slow rate of exchange between external and internal degrees of freedom would keep the internal degrees of freedom from taking up the whole amount of energy and therefore acts as if the effective specific heat were decreased ; this would increase the velocity of sound with increasing frequency. Although few experimental measurements of absorption and dispersion are available it seems probable that this effect exists.

Multimolecular Reactions. The thermal decomposition of ozone has been the subject of several exhaustive investigations. Wulf [32] has pointed out the significance of the observation that when ozone decomposes rapidly, radiation is emitted, part of which lies in the visible and ultraviolet, extending at least as far as 2200 Å. Taking the primary reaction as bimolecular and the heat of decomposition as 34,500 cal., we have the possibility of light of wavelength 4120 Å being emitted ; this is the shortest wavelength that could be emitted from the reaction of two normal molecules. The fact that light of much shorter wavelength is emitted indicates that the reacting molecules possess energy of activation.

Wulf and Tolman [33] have carefully investigated the kinetics of the decomposition in an effort to explain the discrepancies that exist in previous work. They show that the reaction can be made to proceed homogeneously and that it is closely of the second order. It is amazingly sensitive to the presence of traces of catalytic impurities. For ozonized oxygen of low percent ozone the specific second-order rate is inversely proportional to the pressure. This is due to the inhibition by the oxygen and not to a negative catalyst introduced with the oxygen. They discuss their results in

[31] Herzfeld and Rice, *Phys. Rev.*, 31: 691 (1928).
[32] Wulf, *Proc. Nat. Acad. Sci.*, 12: 129 (1926).
[33] Wulf and Tolman, *J. Am. Chem. Soc.*, 49: 1183, 1202, 1650 (1927); *Proc. Nat. Acad. Sci.*, 13: 272 (1927); *cf.* Griffith and McKeown, *J. Am. Chem. Soc.*, 49: 2721 (1927).

the light of the Jahn mechanism which postulates a rapidly estab-
lished equilibrium $O_3 \rightleftarrows O_2 + O$; then follows the slow measured
change $O_3 + O \rightarrow 2O_2$. They find, however, that there are not
enough oxygen atoms present at equilibrium to produce enough
collisions to give the measured rate. The Jahn mechanism in its
original simple form cannot therefore be regarded as tenable.

Hasche [34] has investigated the rate of reaction of nitric oxide
and oxygen; by conducting the reaction in a paraffin-lined vessel
he shows that water is a catalyst, water vapor producing a maxi-
mum increase of speed of 50% over that in a paraffin-lined vessel.
Sulfur dioxide or nitrogen dioxide have no effect on the reaction
rate; an induction period occurs at initial partial pressures of the
reactants below 14 mm. of mercury. The reason for these anoma-
lies has not yet been found.

The decomposition of formic acid is an interesting reaction
owing to the different ways in which the molecule can break up.
Unfortunately from the homogeneous standpoint the acid is very
sensitive to wall catalysis; Nelson and Engelder [35] have shown
that pyrex is least active and etching silica greatly increases its
catalytic activity. The measurements, however, do not permit us
to calculate the fraction of the reaction which occurs in the gas
phase.

Taylor and Wesley [36] have studied the rate of combination of
hydrogen sulfide and sulfur dioxide in pyrex reaction tubes over
a temperature range of 370-730° C. Pyrex glass is a catalyst for
the reaction since the rate was proportional to the surface area
of the reaction chamber. On the other hand the decomposition of
nitrosyl chloride [37] was found to be completely homogeneous
within the limits of experimental error.

[34] Hasche, *J. Am. Chem. Soc.*, **48**: 2253 (1926).
[35] Nelson and Engelder, *J. Phys. Chem.*, **30**: 470 (1926).
[36] Taylor and Wesley, *J. Phys. Chem.*, **31**: 216 (1927).
[37] Taylor and Denslow, *J. Phys. Chem.* **31**: 374 (1927).

Chapter IV.

Thermodynamics of Chemical Reactions.

(Free Energy, Entropy and Heats of Reaction)

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Thermodynamics is usually considered a subject in which the general theory and main lines of application have been fairly well worked out. This year has seen the development of two new additions to the theory and its application which may have the greatest importance. The first of these is Eastman's [1] extension of thermodynamic method to non-isothermal equilibria. The thermocouple, which is an example of such an equilibrium, has been treated previously by several authors, but Eastman has apparently been the first to see full possibilities of extending the ideas inherent in the case of the thermocouple to the general case. He has shown in a general way that the important thermodynamic quantities, entropy, heat and free energy, in cases involving transfer across a temperature gradient are not the same in magnitude nor can they be defined in the same way as the corresponding quantities in the isothermal case. The new quantities which must be used are simply related to these old quantities. His new equations involving these quantities allow for the first time a satisfactory thermodynamic treatment of the Soret effect and of the electrolytic thermocouple. A special advantage of the theory is that it gives a basis for satisfactory experimental determination of the entropy and other thermodynamic properties of the single ions.

Working in a better known field, Kleeman [2] has published a series of papers on the thermodynamics of systems at absolute zero. His most striking result is that the heat of vaporization becomes zero at absolute zero. But the full significance of these papers is not yet fully evident.

[1] Eastman, *J. Am. Chem. Soc.*, **48**: 1482 (1926); **50**: 283, 292 (1928).
[2] Kleeman, *J. Phy. Chem.*, **31**: 747, 937, 1559 (1927).

Giauque [3] has made an interesting suggestion based on the mag- netic properties of the rare earths at low temperatures which may lead to methods of obtaining very low temperatures and which serves to illustrate most strikingly the need of caution in applying the third law to those systems which the mathematical physicist calls degenerate. For example, in the case of a paramagnetic sub- stance, a knowledge of the specific heat curve is not sufficient to define the absolute entropy.

Entropy of Gases. As was the case last year, the determina- tion of the entropy of the simpler gases has claimed the attention of many workers. The missing gaps in the experimental data and also in the theory of the thermodynamic properties of hydro- gen have been filled in.

Cornish and Eastman [4] have determined the specific heat of hydrogen from low temperatures up with the highest accuracy. They used a method depending on the measurement of the velocity of sound. The values obtained fit the theoretical curve admirably and serve conversely to fix experimentally the value for the first rotation energy of the hydrogen molecule with some accuracy.

Condon [5] and later Wang [6] have applied the new wave mechanics of Schrödinger and though there is a slight disagreement in their results due to the different methods of approximation used, both values for the heat of dissociation and electric moment of hydro- gen agree well with the values determined spectroscopically and also, within the limits of error, with the direct value of the heat of dissociation measured calorimetrically by Bichowsky and Cope- land.[7]

It is interesting that atomic hydrogen, whose existence was just beginning to be suspected fifteen years ago, is now tractable to most laboratory measurements and has indeed become of industrial importance, through the development of the atomic hydrogen torch. The history and theory of this torch is interestingly treated by Langmuir.[8]

The other favorite diatomic gas, hydrochloric acid, has been studied by Giauque and Wiebe,[9] who measured the specific heat over a wide range of temperatures together with the heat of in-

[3] Giauque, *J. Am. Chem. Soc.,* **49**: 1864 (1927).
[4] Cornish and Eastman, *J. Am. Chem. Soc.,* **50**: 627 (1928).
[5] Condon, *Proc. Nat. Acad. Sci.,* **13**: 466 (1927).
[6] Wang, *Phys. Rev.,* **31**: 579 (1928).
[7] Bichowsky and Copeland, *J. Am. Chem. Soc.,* **50**: 1315 (1928).
[8] Langmuir, *Ind. Eng. Chem.,* **19**: 667 (1927).
[9] Giauque and Wiebe, *J. Am. Chem. Soc.,* **50**: 101 (1928).

version, heat of melting, and heat of evaporation. The entropy calculated from their measurements agrees with that calculated from the quantum theory and with that measured by E.M.F. methods. Accompanying this paper are two papers on the University of California temperature scale.[10, 11]

In the last report it was noted that the experimental values for the entropy of sodium vapor did not entirely agree with the theory. From the spectroscopist has again come an observation which may resolve the difficulty.[12] There are a series of absorption and emission bands in the sodium spectra which are now known to be due to the Na_2 molecules. The heat of formation of this compound whose existence would surely not have been suspected by the chemist, proves to be low enough so that there is the probability of considerable Na_2 being present in sodium vapor at its normal boiling point. The existence of such a compound would account for the entropy discrepancy (perhaps over account for it); at any event the density of sodium vapor should be determined.

Equilibrium Measurements. Numerous investigations of the equilibrium constant of chemical reactions have been published during the year. Pease and Chesebro [13] have studied the interesting equilibrium $CH_4 + 2H_2O = CO_2 + 4H_2$, using a flow method. Their results give a most welcome verification of the somewhat uncertain determination of the equilibrium $CH_4 = C + 2H_2$ and suggest interesting commercial possibilities.

Krase,[14] calculating from the measurements of Briner, Boner and Rothen,[15] obtains new values for the free energy of NO and hence of a whole series of nitrogen-oxygen compounds. Schott, Swift and Yost [16] have measured the equilibrium $Se + 2I_2 + 3H_2O = H_2SeO_3 + 4HI$, at 25°.

Prescott has continued his studies on equilibrium involving carbides. His latest measurements are on the equilibria $ThO_2 + 4C = ThC_2 + 2CO$ [17] and $2Al_2O_3 + 9C = Al_4C_3 + 6H_2O$.[18]

The measurements of Drummond [19] on the equilibrium of phosphorus and hydrogen to form phosphine, while not apparently of

[10] Giauque, Buffington and Schulze, *J. Am. Chem. Soc.*, **49**: 2343 (1927).
[11] Giauque, Johnston and Kelley, *J. Am. Chem. Soc.*, **49**: 2367 (1927).
[12] Loomis, *Phys. Rev.*, **31**: 323 (1928).
[13] Pease and Chesebro, *J. Am. Chem. Soc.*, **50**: 1465 (1928).
[14] Krase, *J. Phys. Chem.*, **32**: 463 (1928).
[15] Briner, Boner and Rothen, *J. chim. phys.*, **23**: 788 (1926).
[16] Schott, Swift and Yost, *J. Am. Chem. Soc.*, **50**: 721 (1928).
[17] Prescott and Hincke, *J. Am. Chem. Soc.*, **49**: 2744 (1927).
[18] Prescott and Hincke, *J. Am. Chem. Soc.*, **49**: 2744 (1927).
[19] Drummond, *J. Am. Chem. Soc.*, **49**: 1901 (1927).

the accuracy of some other studies, may very well prove to be a *point d'appui* on the free energy of phosphorus compounds.

The equilibria of tin with water and with CO_2 has been studied by Eastman and Robinson,[20] with additional evidence for Eastman's previous conclusion that values of the equilibrium constants for the water-gas reactions are in error.

The industrial applications of thermodynamics are becoming more and more evident; for example, Smith's[21] calculation of the alcohol synthesis. The dissociation pressures of the ammonium orthophosphates have been studied by Warren,[22] leading to methods of preparing these compounds. The industrial chemist must remember that while such measurements may seem only of academic interest, the ammonium phosphates are important fertilizer materials.

Electromotive Force Measurements. Electromotive force measurements will be summarized here insofar as they lead to values of the free energy of formation of substances in their standard states. Auric oxide has been added to the list of available depolarizing materials. Two studies by Gerke and Rourke[23] and by Buehrer and Roseveare[24] on the gold-auric oxide electrode gave values for the free energy of formation of Au_2O_3 of 18810 and 19100 calories.

Nielsen and Brown[25, 26] have studied the electromotive force of various forms of copper and propose the two phase copper amalgam as a standard state. Their studies lead to new values for the free energy of $CuCl_2(aq)$ and CuCl. Getman[27] has measured cells giving the free energy formation and activity of $CdCl_2$, $CdBr_2$, CdI_2 and $CdSO_4$. Cohen,[28] visiting this country, has published measurements on the heat of transition of AgI made by electromotive force methods.

Vapor Pressure Measurements. The following vapor pressure measurements are of interest in connection with free energies: Perry,[29] vapor pressure of methylene chloride; Maass and Maass,[30] vapor pressure and vapor density of SO_2, the vapor

[20] Eastman and Robinson, *J. Am. Chem. Soc.*, **50**: 1106 (1928).
[21] Smith. *Ind. Eng. Chem.*, **19**: 801 (1927).
[22] Warren, *J. Am. Chem. Soc.*, **49**: 1904 (1927).
[23] Gerke and Rourke, *J. Am. Chem. Soc.*, **49**: 1855 (1927).
[24] Buehrer and Roseveare, *J. Am. Chem. Soc.*, **49**: 1989 (1927).
[25] Nielsen and Brown, *J. Am. Chem. Soc.*, **49**: 2423 (1927).
[26] Nielsen and Brown *J. Am. Chem. Soc.*, **50**: 9 (1928).
[27] Getman, *J. Phys. Chem.*, **32**: 91, 940 (1928).
[28] Cohen and Joss, *J. Am. Chem. Soc.*, **50**: 727 (1928).
[29] Perry, *J. Phys. Chem.*, **31**: 1737 (1927).
[30] Maass and Maass, *J. Am. Chem. Soc.*, **50**: 1352 (1927).

pressure and concentration of SO_2 solutions; Millar [31] and Bent and Hildebrand,[32] the vapor pressure of the alkali amalgams; Parks and Barton,[33] the vapor pressure of isopropyl and *tert.*-butyl alcohols; Dana, Burdick and Jenkins,[34] the vapor pressure of vinyl chloride; Jones, Langmuir and Mackay,[35] the vapor pressure of tungsten, molybdenum, platinum, nickel, iron, copper and silver.

Phase Rule Studies. Phase rule studies are: Austin,[36] who has announced the rule that the vapor pressure of two coexisting salt hydrates must be less than that of ice at that temperature; Blasdale and Robson,[37] on the systems H_2O, $MgSO_4$, and H_2O, Na_2SO_4; Robson,[38] H_2O, $MgSO_4$; Hill and Bacon,[39] Na_2CO_3, CO_2, H_2O; Ewing, Krey and Long,[40] $Ca(NO_3)_2$, H_2O.

Heats of Reaction. As has been pointed out, no field of theoretical chemistry has been more neglected in this country than calorimetry. This year produced a respectable number of papers, but these seem to be more or less incidental determinations. There seems to be among the universities, no one interested in carrying on a regular program in calorimetric determinations, such as T. W. Richards initiated. The Bureau of Standards has such a desire but outside support is needed to make this program really effective. Only two papers have been published on the heat of formation: Parks, Hablutzel and Webster,[41] on the heat of formation of ZnO; and Clark and Hetherington,[42] on the heat of formation of ammonium carbamate.

There has been considerable advance in the technique of calorimetry. Steiner and Johnston [43] have described a new calorimeter, on the conduction principle, adapted especially for heats of fusion at elevated temperatures and have measured the heats of transition of ammonium chloride and mercurous iodide, as well as the heat of melting of phenol and benzophenone. Lipsett, Johnson and Maass [44] have shown the advantages of a rotating calorimeter in

[31] Millar, *J. Am. Chem. Soc.,* **49:** 3003 (1927).
[32] Bent and Hildebrand, *J. Am. Chem. Soc.,* **49:** 3011 (1927).
[33] Parks and Barton, *J. Am. Chem. Soc.,* **50:** 24 (1927).
[34] Dana, Burdick and Jenkins, *J. Am. Chem. Soc.,* **49:** 2801 (1927).
[35] Jones, Langmuir and Mackay, *Phys. Rev.,* **30:** 201 (1927).
[36] Austin, *J. Am. Chem. Soc.,* **50:** 333 (1928).
[37] Blasdale and Robson, *J. Am. Chem. Soc.,* **50:** 35 (1928).
[38] Robson, *J. Am. Chem. Soc.,* **49:** 2772 (1927).
[39] Hill and Bacon, *J. Am. Chem. Soc.,* **49:** 2487 (1927).
[40] Ewing, Krey and Long, *J. Am. Chem. Soc.,* **49:** 1958 (1927). Ewing, *J. Am. Chem. Soc.,* **49:** 1963 (1927).
[41] Parks, Hablutzel and Webster, *J. Am. Chem. Soc.,* **49:** 2792 (1927).
[42] Clark and Hetherington, *J. Am. Chem. Soc.,* **49:** 1909 (1927).
[43] Steiner and Johnston, *J. Phys. Chem.,* **32:** 912 (1928).
[44] Lipsett, Johnson and Maass, *J. Am. Chem. Soc.,* **49:** 1940 (1927).

their studies of the heat of solution of finely powdered sodium chloride. They obtain surface energies of 400 ergs per square centimeter which is much smaller than some have assumed. In another paper, the same authors [45] have described a micro-calorimeter with a water equivalent of 1 cc. This calorimeter is adapted especially to heats of solutions. Gucker [46] has described in detail a new calorimeter for measuring the specific heat of aqueous solutions at temperatures up to 80°. Richards, Frevert and Teeter [47] have made a study of the heat of solution in mercury of various two-phase amalgams of cadmium. Sullivan, McGill and French [48] have measured the heat of solution of paraffin in various solvents. Snyder [49] has modified the equation of Kharasch and Sher by the addition of a term covering the heat of combustion of the benzene ring.

Thermodynamics of Solutions. The following papers have been published: Sosnick,[50] method of calculation of partial quantities; Williams, Gabriel and Andrews,[51] hydrolysis of esters and the strength of acids; Cohn, Heyroth and Menkin,[52] dissociation constant of acetic acid; Yost and White,[53] dissociation of per-perosmic acid H_2OsO_5; Chadwell,[54] activity of HCl by freezing point method; Carothers, Bickford and Hurwitz,[55] hydrolysis of certain amines related to aniline; Beans and Kiehl,[56] the hydration of sodium metaphosphate.

[45] Lipsett, Johnson and Maass, *J. Am. Chem. Soc.*, **49**: 925 (1927).
[46] Gucker, *J. Am. Chem. Soc.*, **50**: 1005 (1928).
[47] Richards, Frevert and Teeter, *J. Am. Chem. Soc.*, **50**: 1293 (1926).
[48] Sullivan, McGill and French, *Ind. Eng. Chem.*, **19**: 1040 (1927).
[49] Snyder, *J. Am. Chem. Soc.*, **49**: 2806 (1927).
[50] Sosnick, *J. Am. Chem. Soc.*, **49**: 2255 (1927).
[51] Williams, Gabriel and Andrews, *J. Am. Chem. Soc.*, **50**: 1267 (1928).
[52] Cohn, Heyroth and Menkin, *J. Am. Chem. Soc.*, **50**: 696 (1928).
[53] Yost and White, *J. Am. Chem. Soc.*, **50**: 81 (1928).
[54] Chadwell, *J. Am. Chem. Soc.*, **49**: 2795 (1927).
[55] Carothers, Bickford and Hurwitz, *J. Am. Chem. Soc.*, **49**: 2908 (1927).
[56] Beans and Kiehl, *J. Am. Chem. Soc.*, **49**: 1878 (1927).

Chapter V.

Colloid Chemistry.

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This survey, like those written in 1926 and 1927, deals primarily with the contributions of American chemists to the general theory of colloid chemistry during the past year. Phenomena closely related to colloid chemistry such as contact catalysis, water purification, vulcanization of rubber, tanning, the manufacture of clay products, etc., are considered in separate sections devoted specifically to these subjects. Attention is again called to the Colloid Symposium Monographs, of which volume 5 has recently appeared; volume 6 is in preparation.

Colloidal Solutions. In accord with the view held by many American colloid chemists for almost two decades, Kruyt of Utrecht emphasized the fundamental unity in the theory of colloids.[1] It was pointed out that lyophobic and lyophillic sols are ultimately of the same type. Both are built up of polymolecular particles and the electro-kinetic character of each is the same. It is contended, therefore, that sols are quite different from ionic disperse systems and a theory which seeks for scientific unity by identifying lyophillic colloids with the ionic system is on the wrong track. Important experimental evidence of this view is given by Gortner, Hoffman and Sinclair,[2] who showed that protein "solubility" in neutral salt solutions is, in reality, protein peptization and, as such, is governed as to rate and extent by the nature of the particular anions or cations present in the system. In this peptizing effect there is a pronounced lyotropic or Hofmeister series of anions, the order of increasing peptizing effect being $F < SO_4 < Cl < $ tartrate $< Br < I$. There is a less pronounced

[1] Kruyt, Colloid Symposium Monograph, **5**: 7 (1927).
[2] Gortner, Hoffman and Sinclair, Colloid Symposium Monograph, **5**: 179 (1927).

but still distinct lyotropic series of the cations, the order of increasing peptizing effect being $Na < K < Li < Ba < Sr < Mg < Ca$. Hydrogen ion concentration differences do not account for these lyotropic series as was originally held by Loeb, since the lyotropic effects are observable and measurable even at constant hydrogen ion concentration. Peptization by neutral salts is not hydrolysis for there is no increase in free amino or carboxyl groups.

McBain [3] summarizes the evidence in support of the view that soap solutions must be regarded as colloidal electrolytes.

Stability. Beaver and Muller [4] investigated the effect of ultra-violet light on the stability of gold sols. Bredig's sols are not affected by light. Certain red sols formed by reduction are changed to blue, but prolonged irradiation changes them to stable red sols. The hydrogen ion concentration of the reduction mixture from which the sols are prepared exerts a continuous influence on their color, rate of formation, and photochemical properties. The ion concentration variations accompanying the color changes are interpreted in accordance with Wilson's theory of the constitution of gold sols involving the Donnan equilibrium rather than as an effect of change in degree of dispersion on adsorption equilibria. From investigations on the effect of temperature on the stability of a copper sol Reid and Burton [5] conclude that a sufficient rise in temperature can of itself cause the coagulation of any sol of the dispersoid type and any process of slow coagulation can be changed to rapid coagulation by a definite rise in temperature. The factors involved are: (1) increase in molecular motion, Brownian movement, etc.; (2) change in dielectric constant of the medium; and (3) which is most important, the change in the ionization constant of water.

Sorum [6] prepared a ferric oxide sol free from chloride by hot dialysis of the sol formed by allowing ferric chloride solution to drop slowly into boiling water. This disproves the theory that the ferric oxide sols are to be regarded as complex salts in which ferric chloride acts as a so-called "solution link."

Laird [7] observed the sedimentation of mercury sol, obtaining results in line with the conclusion of Burton [8] and Porter and

[3] McBain, *J. Am. Chem. Soc.,* **50**: 1636 (1928).
[4] Beaver and Muller, *J. Am. Chem. Soc.,* **50**: 304 (1928).
[5] Reid and Burton, *J. Phys. Chem.,* **32**: 425 (1928).
[6] Sorum, *J. Am. Chem. Soc.,* **50**: 1263 (1928).
[7] Laird, *J. Phys. Chem.,* **31**: 1034 (1927).
[8] Burton and Bishop, *Proc. Roy. Soc.,* **100**A: 414 (1922); Burton and Currie, *Phil. Mag.,* **47**: 721 (1924).

Hedges [9] that settling of particles in accord with Smoluchowski's hypsometric law is confined to a thin region near the surface of the sol and that the concentration in the main bulk of the sol remains constant. Mathematical analyses based on the assumption that only gravitational drift and Brownian movement influence the distribution of particles, are offered by Mason and Weaver [10] and by Fürth [11] which are analogous in form but lead to an enormously different conclusion as to the length of time necessary to attain equilibrium.[12]

The coagulation value of colloidal clay was found by Bradfield [13] to vary with slight changes in the hydrogen ion concentration, the concentration of the sol and the nature and extent of the exchange reactions when the electrolyte is mixed with the sol. In coagulation in an alkaline medium, the first step consists in neutralizing the acidity of the clay. The amount of base required for this purpose is directly proportional to the concentration of the clay. The second step consists in neutralization of the clay particles saturated by calcium or potassium.

Peterson and Bartow [14] studied the effect of salts on the rate of coagulation and the optimum precipitation of alumina floc and the importance of this effect in the water purification process.

Hydrophillic Colloids. The lowering of the optical activity of gelatin by potassium halides is attributed by Carpenter [15] to the tautomeric equilibrium between the "gel" and "sol" forms of gelatin, coupled with changes in the hydrol equilibrium of the solvent produced by the added halide salts. Loebel [16] determined the isoelectric point of deaminized gelatin to be at $pH = 4$. The optical rotation, viscosity, surface tension, and foaming of sols were studied as a function of pH. The optical rotation at 10° and the foaming at room temperature are at a maximum at the isoelectric point while the surface tension is a minimum at this point. The viscosity-pH curves show two minima at $pH = 4$ and $pH = 7.3$. Titration with sodium hydroxide is interpreted to indicate a base-combining capacity of 9.7×10^{-4} equivalents per gram. Thomas and Murray [17] deduce the equivalent weight of the so-

9 Porter and Hedges, *Phil. Mag.,* **44**: 641 (1922).
10 Mason and Weaver, *Phys. Rev.,* **23**: 412 (1924).
11 Furth, *Z. Physik,* **40**: 351 (1926).
12 *Cf. also* Kraemer, Colloid Symposium Monograph, **5**: 81 (1927).
13 Bradfield *J. Phys. Chem.,* **32**: 202 (1928).
14 Peterson and Bartow, *Ind. Eng. Chem.,* **20**: 51 (1928).
15 Carpenter, *J. Phys. Chem.,* **31**: 1873 (1927).
16 Loebel, *J. Phys. Chem.,* **32**: 763 (1928).
17 Thomas and Murray, *J. Phys. Chem.,* **32**: 676 (1928).

called arabic acid to be about 1200 from measurements of the base-combining capacity by titration with sodium and barium hydroxide and about 1000 when varying concentrations of alkali and gum arabic are used. The action with bases is attributed to simple chemical combination involving primary valence forces. Similarly, from diffusion potential measurements in hydrochloric acid and gelatin systems, Ferguson and Bacon [18] calculate the equivalent weight of gelatin to be 1090 and conclude that the observations can be accounted for only on the assumption that hydrochloric acid combines in the orthodox chemical fashion with gelatin giving highly ionized gelatin hydrochloride. This is not necessarily the case.[19]

Quartz particles suspended in dilute protein sols under certain conditions move cataphoretically as if the migration were due to a surface consisting of pure protein. Based on this adsorption of protein by quartz Abramson [20] developed a method for studying the mobility of protein. The results for egg albumin at varying pH agree satisfactorily with the values obtained by Svedberg and Tiselius.[21]

Robinson [22] investigated the relation of hydrophillic colloids to winter hardiness in insects. The insects used comprised a hardy, a neutral and a non-hardy species. It was found that the different species gained or lost in bound water in direct proportion to their winter hardiness. Free and so-called bound water were distinguished by the "heat of fusion" method which is based on the fact that free water is all frozen at $-20°$, while bound water is not. The biological significance and the advantages to the species of having the free water transferred into bound water as winter approaches is discussed.

Emulsions. The theory of emulsification proposed by Bancroft [23] was shown by Bancroft and Tucker [24] to have been recognized at least implicitly by Gibbs.[25] The latter pointed out that a film has two surfaces and will therefore have two surface tensions if in contact with the different phases. Gibbs gives a drawing in which it is recognized that these two surface tensions are not necessarily equal. The film will tend to curl toward the

[18] Ferguson and Bacon, *J. Am. Chem. Soc.*, **49**: 1921 (1927); Ferguson, Colloid Symposium Monograph, **5**: 159 (1927).
[19] *Cf.* Weiser, "The Colloidal Salts," 1928.
[20] Abramson, *J. Am. Chem. Soc.*, **50**: 390 (1928).
[21] Svedberg and Tiselius, *J. Am. Chem. Soc.*, **48**: 2272 (1926).
[22] Robinson, Colloid Symposium Monograph, **5**: 199 (1927).
[23] Bancroft, *J. Phys. Chem.*, **17**: 501 (1913).
[24] Bancroft and Tucker, *J. Phys. Chem.*, **31**: 1681 (1927).
[25] Gibbs, "The Scientific Papers of J. Willard Gibbs." Vol. I, 1906.

side having the higher surface tension, hence in all emulsions the dispersed phase is on the side of the film having the higher surface tension. Bancroft rewords the wedge theory of emulsification proposed by Harkins and Hildebrand [26] as follows: "We get oil-in-water if the oriented molecule of the emulsifying agent is chiefly in the water phase and water-in-oil if the oriented molecule is chiefly in the oil phase." When so worded the wedge hypothesis ceases to be an independent hypothesis and becomes a special case in the general theory.

It was pointed out by Finkle, Draper, and Hildebrand [27] in 1923 that solid powders form emulsions when they collect in the interface and one liquid wets the solid better than the other. If enough solid particles are present to fill the interface, the tendency of the interface to contract will cause it to bend in the direction of the more poorly wetted liquid which makes it easy for the latter to become the enclosed phase. Demonstration of the connection between the interfacial contact angle and the type of emulsion is now [28] given by means of microphotographs of emulsions stabilized by solid powders. It is suggested that in forming the emulsion, droplets having the particles chiefly on the outside of the interface would be better protected from coalescing than those having particles on the inside.

Harkins [29] has summarized his extended investigations on the stability of emulsions, monomolecular, and polymolecular films, thickness of the water film on salt solutions and the spreading of liquids.

Fairly stable suspensions of iodine were prepared by Chandler and Miller [30] by rapid acidification with hydrochloric acid of a solution of sodium hypoiodite in the presence of gum arabic at 0°. The emulsion can be concentrated and even dried by adding to it a thick syrup of dextrose or gum arabic from which the water can be evaporated without loss of iodine. A film forms on the surface which alters the evaporation of water but not of iodine. Drying does not cause the iodine particles to coalesce and they are redispersed by shaking with water. A few of the uses of this colloidal iodine as an antiseptic have been given.

Vincent [31] studied the detergent action of soaps and found the

[26] Harkins Davies and Clark, *J. Am. Chem. Soc.*, **31**: 541 (1917).
[27] Finkle, Draper and Hildebrand, *J. Am. Chem. Soc.*, **45**: 2780 (1923).
[28] Scarlett, Morgan and Hildebrand, *J. Phys. Chem.*, **31**: 1566 (1927).
[29] Harkins, Colloid Symposium Monograph, **5**: 19 (1927).
[30] Chandler and Miller, *J. Phys. Chem.*, **31**: 1091 (1927).
[31] Vincent, *J. Phys. Chem.*, **31**: 1281 (1927).

optimum concentration of soaps for the suspension of solids, 0.2-0.4%, to be more than sufficient for the emulsification of oils, this requiring 0.05-0.10%. A concentration of soap above that necessary to cause emulsification is not harmful but beneficial to emulsification. Soap solutions suspend solid material negatively owing to adsorption of negative ions from solution. There is an optimum value for the soap concentration on account of adsorption of positive ions which tends to destabilize the particles. The amount of solid material carried through filter paper (McBain, Harborne and King [32]) by soap solutions should parallel the amount stably suspended (Fall [33]). This is true when the carbon suspensions used by McBain are so treated that the non-stabilized carbon does not retard the passage of the stabilized material through the filter paper. Using the carbon black method of determining deflocculating power Chapin [34] compared the action of soap with that of commercial grades of saponin, acacia, gelatin and casein.

In this connection it was stated in the second volume of the Survey, that Fall used successfully a method suggested by Bancroft to determine the detergent action of soap. This statement is incorrect. Bancroft's proposed method consists essentially in forming a suspension of clay or other solids in soap solution followed by determining the amount of sodium chloride required for coagulation. Fall [33] found that this method was not feasible and so developed a procedure for evaluating detergent action which consists in determining the amount of finely divided MnO_2 which the detergent solutions are able to suspend for a definite length of time.

Gels. Holmes and Maxson [35] have studied the effect of relatively small amounts of water or oleic acid on the formation of soap-turpentine gels.

An investigation of the effect of heating on the structural changes of silica gel was made by Patrick, Frazer and Rush.[36] From measurements of the adsorption of carbon tetrachloride by the heated SiO_2 gel, it was concluded that, between 700 and 800°, the capillaries begin to close but crystallization does not take place below 1100°. It is assumed that some SiO_2 dissolves in the water present in the gel and crystallizes on cooling, thus forming nuclei

[32] McBain, *J. Phys. Chem.*, **28**: 1 (1924).
[33] Fall. *J. Phys. Chem.*, **31**: 801 (1927).
[34] Chapin, *Ind. Eng. Chem.*, **19**: 1275 (1927).
[35] Holmes and Maxson, Colloid Symposium Monograph, **5**: 287 (1927).
[36] Patrick, Frazer and Rush, *J. Phys. Chem.*, **31**: 1511 (1927).

for the crystallization of the rest of the mass at temperatures at which the atoms have sufficient mobility. The gel containing Na_2SO_4 starts to crystallize at lower temperatures.

Rosinger and Vetter [37] describe an apparatus and method for studying the elastic properties of gelatin jellies under static loading conditions. The apparatus can be used also to study the time of relaxation of stretched membranes.

A comprehensive investigation [38] of the optical properties of gelatin-water systems reveals a surprisingly detailed parallelism between optical behavior and colloidal behavior, particularly the capacity to form gels. Gel formation in dilute systems is invariably accompanied by pronounced mutarotation and a high specific rotation. Any agency which prevents the appearance of a high specific rotation prevents gel formation.

Sobotka and Sabin [39] found the rate of diffusion in gels to be a simple function of the concentration of the diffusing solution both in the presence and in the absence of adsorption by the gel. Differences between the rate of diffusion in upward and in downward direction can be observed under certain conditions. The term "barophoresis" is suggested for this phenomenon.

Membranes and Films. Michaelis [40] recognizes five different types of membranes: (1) sieve, such as filter paper; (2) cell filters, such as very fine filter paper; (3) bacterial filters, such as kieselguhr; (4) colloidal filters, such as parchment and collodion; and (5) molecular sieve filters, such as copper ferrocyanide. Michaelis fails to distinguish an ultrafilter, which acts like a sieve, from a semipermeable membrane, which functions owing to strong negative adsorption. He therefore designates copper ferrocyanide and hardened collodion containing very fine pores as molecular sieve membranes, the pores of which are assumed to be large enough to allow certain atoms or molecules to pass and not others. Bancroft and Nugent [41] conclude that straight filtration by the kidneys plays little or no part in effecting the changes in concentration actually observed in the urine and that the concentration changes do not correspond to equilibrium conditions. "Salting out" effects, negative osmose, initial osmotic flow, and the special nature of the

[37] Rosinger and Vetter, *J. Am. Chem. Soc.*, **49**: 2994 (1927).
[38] Kraemer and Fanselow, *J. Phys. Chem.*, **32**: 910 (1928).
[39] Sobotka and Sabin, *J. Am. Chem. Soc.*, **50**: 561 (1928).
[40] Michaelis, Colloid Symposium Monograph, **5**: 135 (1927).
[41] Bancroft and Nugent, Colloid Symposium Monograph, **5**: 149 (1927).

membrane are recognized as important factors but the extent to which each enters in, is not known.

Stamm [42] showed that dilute alkalies increase the rate of electro-endosmose through wood membranes and dilute acids decrease it, giving a straight-line relation between rate and pH. Dilute acids affect the membrane permanently probably owing to hydrolysis on the internal surface which reduces the rate of flow. Aqueous salt solutions show the normal effect of salts with different valent cations and anions on negatively charged membranes. Tri- and tetravalent cations reverse the direction of flow and the sign of the contact potential while polyvalent anions increase the rate of flow and the negative potential. Divalent cations cause a maximum in the rate of flow at a lower concentration than for univalent cations. Determination of the ζ potential on cellulose by means of a "streaming potential" method devised by Briggs [43] indicates that the ζ potential varies with the source and history of the sample of cellulose. For two samples of rag pulp and for a wood pulp, the respective values are 0.0214, 0.0161, and 0.0083 volts.

Kurtz [44] contests the common assumption that plastic films developed during the formation of a drop suspended from a tip would increase the drop size and the apparent interfacial tension. He also contests its corollary, that plastic films can never be the cause of low apparent interfacial tensions.

Continuing his investigations on structural colors in insects Mason [45] showed that metallic iridescent insect integuments owe their color phenomenon to a thin laminated layer at or just beneath the surface which acts as a multiple thin film. Enameled iridescent integuments owe their color to a thick multiple-film layer the properties of which are modified by the closely spaced minute rods which perforate it. Surface color is not exhibited by iridescent insect integuments.

Adsorption. *Gibbs on Adsorption.* From the work of Gibbs, Bancroft [24] showed that the necessary and sufficient criterion for the applicability of the Freundlich equation to the adsorption of a gas by a liquid in which the gas is practically insoluble, is that the change of surface tension is proportional to the change of adsorption. The exponent n in Freundlich's equation is a measure of the change in the surface tension with the adsorp-

[42] Stamm, Colloid Symposium Monograph, **5**: 361 (1927).
[43] Briggs, *J. Phys. Chem.*, **32**: 641 (1928).
[44] Kurtz, *J. Am. Chem. Soc.*, **49**: 1991 (1927).
[45] Mason, *J. Phys. Chem.*, **31**: 1856 (1927).

tion by a liquid adsorbent. For Freundlich's equation to apply to the adsorption of a gas by a solid, all that seems necessary is that the change of the surface tension or some equivalent property is proportional to the change of adsorption.

McBain and Davies [46] made precise measurements of the absolute adsorption at the air-liquid interface of solutions of *p*-toluidine, amyl alcohol and camphor. In every case the amounts adsorbed are several times greater than that corresponding to a monomolecular film. It is concluded, therefore, that for such solutions over a wide range of concentration of solution the surface consists of a saturated monomolecular film of solute resting on a comparatively thick layer of concentrated solution, gradually falling off with depth to the bulk concentration. Chains of oriented molecules are assumed to extend downward into the solutions from the outermost monomolecular film. The so-called concentration formula of Gibbs usually quoted gives erroneous values for adsorption. To obtain corrected values it is necessary to employ the true thermodynamic formula of Gibbs and to take into account not only all the components, which are usually more numerous than anticipated, but also to include the electrical effects which always occur at surfaces but are not included in the Gibbs' equation.

Adsorption by Charcoal and Hydrous Oxides. Miller [47] has summarized his important observations on adsorption from solutions by ash-free charcoal. [48] The adsorbent exhibits the following properties : It adsorbs acids but not inorganic bases, the strong inorganic bases being negatively adsorbed. It adsorbs salts hydrolytically, the adsorption being exclusively hydrolytic, for such salts as NaCl and K_2SO_4, acid alone being taken up. The adsorption of salts of strongly adsorbed organic acids, such as sodium benzoate, is partly hydrolytic and partly molecular. Anomalous results, reported on adsorption by unpurified charcoal, were traced to the impurities. Additional evidence is presented to show that orientation of molecules is involved in the adsorption. To illustrate, the position of the hydroxyl and amino groups in hydroxy- and aminobenzoic acids influences markedly the adsorption of these acids. Adsorbed acids on charcoal are found to be incapable of inverting

[46] McBain and Davies, *J. Am. Chem. Soc.*, **49**: 2230 (1927).
[47] Miller, Colloid Symposium Monograph, **5**: 55 (1927).
[48] Miller, *J. Phys. Chem.*, **30**: 1031, 1162 (1926); **31**: 1197 (1927); Bartell and Miller, *J. Am. Chem. Soc.*, **45**: 1106 (1923); Miller, *J. Am. Chem. Soc.*, **46**: 1150 (1924); **47**: 1270 (1925); Miller and Bandemer, *J. Am. Chem. Soc.*, **49**: 1686 (1927); *J. Phys. Chem.*, **32**: 829 (1928).

sugar. Apparently the adsorbed acids exist in direct molecular contact with the surface atoms of the charcoal and are undissociated. This non-dissociation may explain the fact that acids decrease but do not increase the negative charge on charcoal in cataphoresis and electro-endosmose experiments. The negative charge of carbon in alkaline solution cannot be due to adsorption of hydroxyl ion since the latter ion is negatively adsorbed. By adsorption from buffer solutions it was shown that pure charcoal does not have an isoelectric point and that the isoelectric point for blood charcoal is also fictitious.

In opposition to Miller's view that neutral inorganic salts such as sodium chloride are hydrolytically adsorbed, Parks and Bartlett [49] obtained no evidence of such hydrolytic adsorption with an ash-free activated charcoal. The hydrogen ion of inorganic acids and the hydroxyl ion of inorganic bases are most strongly adsorbed. The order of anion adsorption was found to be $NO_3 >$ $Cl > SO_4$. The phenomena are explained on the basis of the attraction of ions by colloidal particles and the effect of mass action on this attractive force. It is hoped that we may have shortly an explanation for the discrepancies in the observations of Miller and of Parks and Bartlett.

The effect of hydrogen ion concentration on the adsorption by nonpurified and technical charcoal was studied by Hauge and Willaman.[50] It was found that the more acid the solution, the stronger the adsorption of negative sols, such as caramel and benzopurpurin, while alkalinity favors the adsorption of positive ions, such as methylene blue cation. The adsorption of proteins is at a maximum in the general region of the isoelectric point of the protein. In technical practice the following factors should be considered: the electrical properties of the substance to be adsorbed; the electrical properties of available carbons; and the permissible pH of the solutes used.

Lowry and Olmstead [51] developed a theory of adsorption which makes it possible to calculate quite accurately the adsorption of a gas at any temperature and pressure by a given adsorbent, if the distribution of adsorption potential with volume for the gas and adsorbent is first determined. The "adsorption potential" represents the energy required to compress a gram molecule of the gas atmosphere to the density at which some small mass exists

[49] Parks and Bartlett, *J. Am. Chem. Soc.*, **49**: 1698 (1927).
[50] Hauge and Willaman, *Ind. Eng. Chem.*, **19**: 943 (1927).
[51] Lowry and Olmstead, *J. Phys. Chem.*, **31**: 1601 (1927).

on the surface of the adsorbent. The applicability of the formulation is illustrated by data on the adsorption of carbon dioxide by carbon.

Pearce and McKinley [52] describe a calorimetric method for the accurate determination of heats of adsorption and the heats of adsorption of some vapors on charcoal were measured at 25°. Coolidge [53] found that charcoal adsorbs small amounts of mercury vapor at high temperature, but the adsorption is negligible at room temperature. The amount adsorbed decreases with rising temperature when the vapor is kept at constant pressure but increases with rising temperature when the vapor is kept saturated. The heat of adsorption was found to be smaller than the heat of evaporation. Leopold and Johnston [54] studied the rate of absorption of water by bakelite.

Grettie and Williams [55] determined the extent to which 18 pure organic compounds are adsorbed from $0.01M$ solution on fuller's earth and on the hydrous oxides of silicon, aluminum, and iron. The extent of adsorption on silica is roughly proportional to their basic strengths and on alumina, roughly proportional to their acidic strengths. Adsorption values with hydrous ferric oxide shows no regularity, possibly owing to impurities in the adsorbent. Klosky and Burggraff [56] measured the adsorption of sulfur dioxide by titania gel at -22.5, 0, 25, and 50°. The results over the whole range are best represented by Polanyi's formula.

Adsorption of Dyes. Preliminary to a study of the mechanism of color-lake formation, Weiser and Porter [57] investigated the effect of hydrogen ion concentration on the adsorption of an inorganic ion sulfate and an organic ion oxalate, both separately and simultaneously, by the hydrous oxides commonly employed as mordants. Increasing the hydrogen ion concentration raises the charge on the particles, thereby increasing their capacity to adsorb anions. The adsorption of the latter falls off quite rapidly but regularly on the alkaline side of the neutral point. Observations on simultaneous adsorption disclose that oxalate is adsorbed much more strongly than sulfate, the adsorptions being equal in neutral solution when the ratio of the sulfate to the oxalate concentration

[52] Pearce and McKinley, *J. Phys. Chem.*, **32**: 360 (1927).
[53] Coolidge, *J. Am. Chem. Soc.*, **49**: 1949 (1927).
[54] Leopold and Johnston, *J. Phys. Chem.*, **32**: 876 (1928).
[55] Grettie and Williams, *J. Am. Chem. Soc.*, **50**: 668 (1928).
[56] Klosky and Burggraff, *J. Am. Chem. Soc.*, **50**: 1045 (1928).
[57] Weiser and Porter, *J. Phys. Chem.*, **31**: 1383, 1704, 1824 (1927); Colloid Symposium Monograph, **5**: 369 (1927).

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is 128 to 1. These observations were followed by similar studies on the taking up of the acid dyes, alizarin S.W., alizarin, and orange II, and the basic dye, methylene blue, by the hydrous oxide mordants. In every case the lake formation process consists in the adsorption of the colored ion by the hydrous oxide, no indication being obtained of the formation of definite compounds at any pH value. The effect of pH on the adsorption of the dye ions is comparable throughout to the adsorption of sulfate and oxalate provided the dye remains soluble. Marker and Gordon's [58] conclusion that at low pH values ferric oxide and alumina react with orange II to form salts, appeared to be disproven. The presence of a high concentration of sulfuric acid in the bath prevents the adsorption of the dye and causes it to be precipitated as the corresponding free acid, giving mixtures which are not lakes. The effect of sulfate on the adsorption of alizarin is very similar to its effect on oxalate, sulfate replacing the dye in part if the bath is acid, this replacing action decreasing to zero as the bath becomes alkaline. The effect of calcium ion on the formation of alizarin lakes is to increase the charge on the mordant, thereby enabling it to adsorb more of the dye anion from the alkaline bath, rather than to remove sulfate or to form a complex calcium aluminum alizarate. In general, the presence of a strongly adsorbed cation in the dye bath increases the rate and quantity of adsorption of acid dyes and has an opposite effect on basic dyes, its effect increasing with the pH of the bath and with its own concentration. The presence of a strongly adsorbed anion in the dye bath decreases the rate and quantity of adsorption of acid dyes and increases the adsorption of basic dyes, its effectiveness increasing with the acidity of the solutions and with its own concentration. If the dye bath is either acid or basic, the effect of the cations and anions are practically independent of each other, the influence of the cation predominating in the basic baths and the anion in acid baths.

White and Gordon [59] attribute the cutting down by phosphate of the adsorption of orange II by mordants to the formation of a compound with the gels which is so insoluble that it does not furnish any metal ions to react with the dye and form a metal dye compound. Since Weiser and Porter claim that the mechanism of the formation of iron and alumina lakes of orange II, proposed by Gordon and his collaborators, is experimentally unsound,

Marker and Gordon, *J. Ind. Eng. Chem.*, **16**: 1185 (1924).
[59] White and Gordon, *J. Phys. Chem.*, **32**: 380 (1928).

Gordon's theory of the action of phosphate in the process is open to question.

Yoe and Hill [60] investigated the factors influencing the formation of the alumina lakes of the ammonium salt of aurinitricarboxylic acid and sodium alizarin monosulfate, with reference to their use in the colorimetrical estimation of small amounts of aluminum in water.

In this connection, mention should be made of some observations of Sheppard and Crouch [61] on the optical sensitizing action of silver halide emulsions by the adsorption of such dyes as orthochrome T. It is assumed that the dye cation is adsorbed to the bromide ions of the silver bromide surface, owing to electrostatic attraction. If this electrostriction passes into homopolar combinations in agreement with the conclusion that the colored form which does the sensitizing is less polar than the colorless, then on adsorption of light, an electron is freed, possibly from the bromide ion and a silver ion is reduced directly, or indirectly by the "reduced" dye cation. Weiser and Garrison [62] attribute the increased photochemical sensitivity of zinc sulfide in the presence of zinc salts of univalent anions to adsorbed zinc ions. Salts containing anions which are more readily adsorbed than the cations reduce or prevent the darkening of zinc sulfide by light.

Houck [63] found the dyeing of silk by acid and basic dyes to be a typical adsorption phenomenon. The strongly adsorbed sulfate ion cuts down the adsorption of acid dyes and increases the adsorption of basic dyes. The adsorption of acid dyes is greater in acid than in neutral or basic solution. Silk adsorbs tannin, more being taken up from hot solution than from cold. No explanation is offered for the effect of temperature on the adsorption. Tannins are coagulated by mineral acids and the volume apparently increases with increasing acid concentration. The volumes of tannin coagulated do not necessarily represent the true effect of the electrolyte because of experimental errors that cannot be readily evaluated. [64]

Adsorption and Crystal Form.   Saylor [65] points out that sodium chloride crystallizes ordinarily in cubes but the presence of urea causes the appearance of octahedra. This is due to selective ad-

[60] Yoe and Hill, *J. Am. Chem. Soc.*, **49**: 2395 (1927); **50**: 748 (1928).
[61] Sheppard and Crouch, *J. Phys. Chem.*, **32**: 751 (1928).
[62] Weiser and Garrison, *J. Phys. Chem.*, **31**: 1237 (1927).
[63] Houck, *J. Phys. Chem.*, **32**: 161 (1928).
[64] Thomas and Foster, *Ind. Eng. Chem.*, **14**: 191 (1922).
[65] Saylor, Colloid Symposium Monograph, **5**: 49 (1927).

sorption, but it is difficult to prove what portions of a sodium chloride crystal adsorb urea strongly. The problem has been made general and solved by an indirect method. If we have a substance which can crystallize from aqueous solution in two forms, and it is allowed to crystallize once in the presence of a strongly adsorbed anion and once in the presence of a strongly adsorbed cation, one or the other of the two solutions will show an increased tendency to give the less stable form. This was illustrated by allowing NaCl to crystallize once from acid and once from alkaline solution. Octahedra are formed in alkaline solution, indicating that urea is adsorbed on the same face as hydroxyl ion. Alcohol cuts down the adsorption of anions so that cubes are formed from an alkaline solution containing alcohol.

In a discussion of colloids on the electrodeposition of metals Blum [66] assumes that the union of one or more electrons with a positive ion takes place on the cathode surface at a point deter- mined both by the orientation of the metal atoms on the cathode surface and by the effective concentration of the metal ions in the cathode film. When this ionic concentration is high the cathode polarization will be low and conditions will be favorable for the growth of existing crystals and vice versa. According to this theory any changes which increase cathode polarization will make changes in the type of crystal structure in the oxide from fibrous to conical to broken and, finally, to spongy and powdery deposits. Colloids tend to produce the latter two types which leads to the conclusion that the principal effects of colloids on crystal struc- ture are associated with increase in the cathode polarization which they produce. The specific effects of colloids, especially their tend- ency to produce characteristic growths, may be due to this selective adsorption on different crystal faces.

Adhesion. For determining the adhesion tension liquid against solid, Bartell and Osterhof [67] have developed a method which in- volves the measurement of the pressure of displacement of one liquid by another. The adhesion tension was determined for a number of liquids against carbon and silica. The work of adhesion was also determined and the pressure of adsorption was calculated from the expression $Wa/Wc \times$ internal pressure, where Wa is the work of adhesion and Wc the work of cohesion. Thus, the adsorp- tion pressure of water on carbon is 10,900 atmospheres if the

[66] Blum, Colloid Symposium Monograph, 5: 301 (1927).
[67] Bartell and Osterhof, Colloid Symposium Monograph, 5: 113 (1927).

internal pressure of water is 12,450 atmospheres. It is concluded that those compounds which have a structure favorable to high adsorption show high adhesion values. In the case of a polar hydrocarbon, the molecular orientation is apparently such that the more polar group is in contact with the silica.

Nietz [68] investigated seventy organic substances for contact angle, effect on the surface tension of water, spreading, and work of adhesion. In all cases the results appear to be in accord with other results on liquids and solids and with the theories proposed by Harkins and Langmuir. It was shown that some substances which spread violently on liquids do not affect their surface tension very greatly. Substances which do not spread do not lower the surface tension. When the work of adhesion [69] of the saturated fatty acids for water is plotted against the number of carbon atoms, the adhesional work shows a marked minimum in the neighborhood of 12 to 14 carbon atoms beyond which there is a very pronounced increase. The general trend of the curve is attributed partly to the general nature of the adhesional energy-temperature relations and partly to the mechanical effects of the length of the carbon chain. Alternating effects shown by odd and even acids and the two sets of values for α and β odd acids are attributed to differences in crystal structure.

Washburn [70] showed that when an evaporating solution wets the walls with which it is in contact it will rise on them above the body of the liquid. Crystallization sets in forming a crust which is not in actual contact with the supporting walls, leaving a capillary space through which the solution creeps to a new height. If the liquid does not wet the surface at all there is no creeping; if it wets it even a little, in other words, if the adhesion between the liquid and the solid is greater than the cohesional force of the liquid, the liquid will climb, and on evaporating will build a capillary through which it will rise higher.

Observations by McBain and Lee [71] on adhesives such as gums, resins and waxes between polished metal surfaces disclose that the thinner the layer of adhesive the stronger the joint. The effect of thickness is not appreciable with very thick films but is marked with very thin films. The rule is confirmed that a parallelism exists between the strength of a joint between smooth, metallic surfaces

[68] Nietz, *J. Phys. Chem.*, **32**: 255 (1928).
[69] Nietz, *J. Phys. Chem.*, **32**: 620 (1928).
[70] Washburn, *J. Phys. Chem.*, **31**: 1246 (1927).
[71] McBain and Lee, *J. Phys. Chem.*, **31**: 1674 (1927).

and the mechanical and intrinsic properties of the metals them-
selves. The mechanical properties of a number of adhesive films
have been described.[72] For measuring the adhesive strength be-
tween an abrasive and a glue, Lanyon [73] recommends determin-
ing the breaking strength of briquettes made from the abrasive
and the glue solution.

Plasticity. Bingham [74] recognizes three types of plastic flow:
(1) a suspension of a very finely divided solid in a viscous
medium, such as fats and greases; (2) polar colloids, such as a
solution of nitrocellulose in dibutyl phthalate; and (3) the flow of
single crystals along slip planes. Browne and Brouse [75] discuss the
consistency of casein glue with and without lime and the effect
of such factors as alkalinity and concentration on the viscosity of
casein glue. Sheppard, Carver and Houck [76] report the nature of
solvents for cellulose esters without touching on the relationship
between mechanical structure and plasticity. To account for the
solubility of nitrocellulose the polar-non-polar theory of Highfield
is taken as a working hypothesis. For example Highfield assumed,
with good evidence, that one particular mixture of acetone and
water has the optimum polar characteristics for dissolving nitro-
cellulose. In general, it is assumed that for every cellulose ester
there is some particular polarity which the solvent must have to
peptize it thoroughly. Since it is unlikely that any pure liquid
would have exactly the proper degree of polarity, to make the best
solvent, a neutral mixture of two liquids one of which has a
polarity too great and the other too small will furnish the optimum
conditions for maximum peptization.

Giesy and Arzoomanian [77] describe a rapid extrusive type
plastometer; Phipps [78] discusses the use of the falling sphere
viscosimeter as a plastometer; and Speicher and Pfeiffer [79] discuss
the falling ball method for measurement of the apparent viscosity
of nitrocellulose solutions.

[72] McBain and Lee, *Ind. Eng. Chem.*, **19**: 1005 (1927).
[73] Lanyon, *Ind. Eng. Chem.*, **19**: 1191 (1927).
[74] Bingham, Colloid Symposium Monograph, **5**: 219 (1927).
[75] Browne and Brouse, Colloid Symposium Monograph, **5**: 229 (1927).
[76] Sheppard, Carver and Houck, Colloid Symposium Monograph, **5**: 243 (1927).
[77] Giesy and Arzoomanian, Colloid Symposium Monograph, **5**: 253 (1927).
[78] Phipps, Colloid Symposium Monograph, **5**: 259 (1927).
[79] Speicher and Pfeiffer, Colloid Symposium Monograph, **5**: 267 (1927).

Chapter VI.

Catalysis.

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In attempting a review of the studies in catalysis which have been reported during the past twelve months, one is confronted at the start with the problem of selecting the investigations which ought to be included. As Reid[1] pointed out in presenting the Fifth Report of the Committee on Contact Catalysis, the distinction between catalyzed and non-catalyzed reactions is becoming less obvious. He ventured the opinion that soon all reactions will be catalytic and then this term will cease to be descriptive. The review which follows may, therefore, contain reference to investigations in which the phenomenon of catalysis is not all-important. On the other hand reports may have been omitted which, though not primarily concerned with this subject matter, are nevertheless distinct contributions. For such inclusions and omissions apologies are offered.

Catalytic Oxidation. Three investigations of the catalytic synthesis of water have been reported during the past year. Benton and Elgin[2] continued their study of the mechanism of this reaction, considering specifically the catalytic action of gold. They found that gold differed markedly from silver which they had previously examined. They were unable to offer any simple explanation for the catalytic action of gold. Smith[3] also studied the direct synthesis of water, employing copper, nickel, copper and nickel mixtures, and copper and aluminum as contact materials. He attempted to correlate the oxide which forms on the surface of these catalysts with their catalytic activity. He found that the most active catalysts also formed the greatest amount of oxide

[1] Reid, *J. Phys. Chem.*, **31**: 1121 (1927).
[2] Benton and Elgin, *J. Am. Chem. Soc.*, **49**: 2426 (1927).
[3] Smith, *J. Phys. Chem.*, **32**: 719 (1928).

during the catalysis. Smith has suggested a mechanism which in- volves the interaction of hydrogen molecules and activated oxygen molecules or atoms. A stable form of oxide formed during the synthesis probably contributes very little to the catalysis. In fact, it may retard the reaction by monopolizing a portion of the cata- lyst surface. In considering a variety of reactions which might be catalyzed by metallized silica gels as developed by Reyerson, he, together with Swearingen,[4] has also considered the synthesis of water. He investigated gels containing silver, copper, platinum, and palladium.

Reyerson and Swearingen[5] have extended their examination of metallized silica gels to the reaction involved in the oxidation of methane. In this study they employed silica gels coated with copper, platinum and palladium, each one of which they found accelerated the oxidation of methane. Coward and Guest[6] have reported an interesting investigation involving the air oxidation of natural gas. They were primarily concerned with the tempera- ture of ignition of natural gas-air mixtures when brought in con- tact with heated metals. They found that what they considered to be strongly catalytic surfaces had to be heated to higher tem- peratures in order to ignite explosive mixtures of natural gas and air than proved to be the case when a less active surface is in- volved. The results of a study of the negative catalytic effect of salts of the alkali metals on combustion have led Thomas and Hochwalt[7] to suggest the use of such alkali salts in extinguishing oil and wood fires. These investigators found that the effectiveness of the various alkali salts considerably increases with the increase in atomic weight of the alkali metal.

Two very interesting papers have been presented on ammonia oxidation. In one by Parsons,[8] ammonia oxidation plants are de- scribed with considerable detail. Production costs are an important consideration in this paper. Taylor[9] has also discussed the prac- tical aspects of ammonia oxidation, including with his report a brief statement of the theoretical considerations involved. A paper by King[10] may be included at this point. King measured the effect of various salts on the velocity of oxidation of ammonia by per-

[4] Swearingen and Reyerson, *J. Phys. Chem.,* **32:** 113 (1928).
[5] Ryerson and Swearingen, *J. Phys. Chem.,* **32:** 192 (1928).
[6] Coward and Guest, *J. Am. Chem. Soc.,* **49:** 2479 (1927).
[7] Thomas and Hochwalt, *Ind. Eng. Chem.,* **20:** 575 (1928).
[8] Parsons, *Ind. Eng. Chem.,* **19:** 789 (1927).
[9] Taylor, *Ind. Eng. Chem.,* **19:** 1250 (1927).
[10] King, *J. Am. Chem. Soc.,* **49:** 2689 (1927).

sulfate when this reaction is catalyzed by silver ions. He was particularly interested in the specific effect of ions of potassium, sodium, hydroxyl and nitrate. Their effect was apparently in accord with their action on the activity coefficient of other ions, as indicated by solubility and other measurements.

Lewis and Ries [11] have reexamined the reaction rates involved in the synthesis of SO_3 from SO_2 and oxygen. They have developed an expression by means of which the conversion to SO_3 can be accurately determined for a variety of operating conditions. An interesting catalyst suitable for use in the synthesis of SO_3 has been described by Nickell.[12] It is essentially a complex vanadium silicate which is said not to be poisoned by arsenic compounds or hydrochloric acid.

Bitler and James [13] have described very briefly a plant in which they are oxidizing oil vapors catalytically. Simington and Adkins [14] have studied the air oxidation of ethyl, isopropyl and butyl alcohols over a large number of catalysts. They obtain aldehyde, ketone, acid, carbon dioxide, carbon monoxide, and saturated and unsaturated hydrocarbons. In an attempt to modify the catalytic action of the various metals investigated, small amounts of various materials which might possibly have some "promotor action" were added. In no case, however, was there any marked effect produced. Milas [15] has presented the results of an investigation of the oxidation of primary alcohols. He found that vanadium pentoxide in dilute sulfuric acid accelerates the oxidizing action of chlorates on methyl, ethyl, n-propyl, n-butyl, isobutyl and isoamyl alcohols, acetal and mixtures of paraldehyde and ethyl alcohol, and paraldehyde and n-butyl alcohol to give esters. In a second paper he reported [16] an investigation of the reaction of vanadium pentoxide, also osmium oxide, in the oxidation of furfural and pyromucic acid. The nature of the oxidation products and the probable mechanism are discussed. The catalytic action of vanadium pentoxide has also been considered by Sessions.[17] He found that when furfural is oxidized in contact with this material, maleic acid and maleic anhydride, formaldehyde, carbon dioxide and water are formed. The best results were obtained at catalyst temperatures

[11] Lewis and Ries, *Ind. Eng. Chem.*, **19**: 830 (1927).
[12] Nickell, *Chem. Met. Eng.*, **35**: 153 (1928).
[13] Bitler and James, *Chem. Met. Eng.*, **35**: 156 (1928).
[14] Simington and Adkins, *J. Am. Chem. Soc.*, **50**: 1449 (1928).
[15] Milas, *J. Am. Chem. Soc.*, **50**: 493 (1928).
[16] Milas, *J. Am. Chem. Soc.*, **49**: 2005 (1927).
[17] Sessions, *J. Am. Chem. Soc.*, **50**: 1696 (1928).

of 200-300° C., but even under the most optimum conditions, yields were very small. Walton and Graham [18] have determined the effect of iron and copper salts on the oxidation of several dicarboxylic acids by hydrogen peroxide. They observed, for example, that oxalic acid tended to inhibit the decomposition of hydrogen peroxide when ferric chloride was employed. They accounted for this on the assumption that the oxalic acid combines with the ferric ion in the presence of hydrogen peroxide to form a stable complex in which there is one mol of the ferric ion for each mol of the oxalate. Experimental evidence is offered to support this contention.

In 1923 Bray and Livingston [19] showed that the catalytic decomposition of hydrogen peroxide in hydrobromic acid solutions was due to the simultaneous oxidation and reduction of the peroxide by bromine and by bromide ion. These investigators [20] have recently reported a further consideration of this earlier work in which they offer an equation for the rate of reduction of bromine by hydrogen peroxide. Ort [21] has studied the inhibiting action of insulin on the action of hydrogen peroxide on dextrose and levulose in the presence of certain amino acids. It is interesting to note that insulin was found to have a definite retarding action when either dextrose or levulose were involved. When a mixture of these sugars was employed, however, the insulin apparently had no marked effect.

Catalytic Reduction. Reyerson and Morris have made two reports of hydrogenation reactions catalyzed by metallized silica gels. In one [22] a silica gel containing copper is shown to possess appreciable activity in the hydrogenation of ethylene. In the other [23] they show that ethylene and ethane are produced when acetylene and hydrogen are contacted with silica gels containing palladium, platinum and copper. The catalytic activity increased in the order in which the metals are given. Pease and his coworkers have also presented two papers on the hydrogenation of ethylene. In one by Pease and Stewart [24] the action of supported catalysts containing iron, cobalt, nickel, copper and silver as the active ingredients was determined. They observed a periodicity

[18] Walton and Graham, *J. Am. Chem. Soc.,* **50**: 1641 (1928).
[19] Bray and Livingston, *J. Am. Chem. Soc.,* **45**: 1251 (1923).
[20] Bray and Livingston, *J. Am. Chem. Soc.,* **50**: 1654 (1928).
[21] Ort, *J. Am. Chem. Soc.,* **50**: 420 (1928).
[22] Morris and Reyerson, *J. Phys. Chem.,* **31**: 1220 (1927).
[23] Morris and Reyerson, *J. Phys. Chem.,* **31**: 1332 (1927).
[24] Pease and Stewart, *J. Am. Chem. Soc.,* **49**: 2783 (1927).

among these metals in their catalytic properties and also a correlation with their ability to form complex ions. Pease and Harris [25] have reported experiments involving ethylene and hydrogen in which copper was the catalyst. These authors conclude that the reaction is very nearly bimolecular at 220° C.

Several investigations have been reported involving the catalytic reduction of organic compounds in solution. Glattfeld and Shaver [26] studied the catalytic reduction of *d*-gluconic acid to *d*-glucose in aqueous solution in the presence of a platinum oxide catalyst. Glucosazone, glucose oxime, and crystalline *d*-glucose were identified. Brown, Etzel, and Henke [27] studied the catalytic reduction of organic nitro compounds in a liquid system. They reduced quantitatively such nitro compounds with hydrogen at 500 lbs. pressure employing reduced nickel oxide as a catalyst. Etzel [28] has also studied the reduction of nitrobenzene when catalyzed by titania. Aniline, azobenzene, hydrazobenzene, ammonia and cyclo-compounds were obtained. The best yield of aniline was 94.4%, obtained when the catalyst temperature was 282° C. The temperature at which the catalyst was reduced appeared to influence the results. Adams has reported further work on catalytic reduction by means of a platinum oxide-platinum black catalyst. Together with Bray,[29] he studied the action of hydrogen in the presence of this catalyst on furfuracrolein in alkaline solutions, considering particularly the promotor action of ferrous sulfate alone and ferrous sulfate together with zinc acetate. Brown, Brothers and Etzel [30] studied the hydrogenation and nitrobenzene when contacted with metallic thallium. They found thallium on asbestos to be an excellent catalyst for the production of azobenzene. The best results were obtained at 260° C. Iki [31] has described an electric corrosion method for preparing nickel catalysts, which he holds to be very reactive when employed in the hydrogenation of oils.

Hydrolysis. In a consideration of the hydrolysis of esters in aqueous solutions, Terry [32] has formulated the action of hydrochloric acid and of potassium hydroxide and of sodium hydroxide in this type of reaction. She has given expressions which represent

[25] Pease and Harris, *J. Am. Chem. Soc.*, **49:** 2503 (1927).
[26] Glattfeld and Shaver, *J. Am. Chem. Soc.*, **49:** 2305 (1927).
[27] Brown, Etzel and Henke, *J. Phys. Chem.*, **32:** 631 (1928).
[28] Etzel, *J. Phys. Chem.*, **32:** 852 (1928).
[29] Bray and Adams, *J. Am. Chem. Soc.*, **49:** 2101 (1927).
[30] Brown, Brothers and Etzel, *J. Phys. Chem.*, **32:** 456 (1928).
[31] Iki, *Ind. Eng. Chem.*, **20:** 472 (1928).
[32] Terry, *J. Am. Chem. Soc.*, **50:** 1239 (1928).

the influence of these catalysts at varying concentrations, expressions which she considers to describe correctly the catalytic activity of these substances even in the presence of neutral salts. In a second paper Terry and Stieglitz [33] have reported measurements on the velocity of saponification of ethyl acetate by sodium hydroxide in aqueous solutions of various concentrations and temperatures. Harned and Hawkins [34] have studied the velocity of hydrolysis of ethyl acetate in a number of salt solutions when catalyzed by dichloroacetic acid. They also considered the hydrolysis of ethyl formate when catalyzed by monochloroacetic acid. Williams, Gabriel, and Andrews [35] examined the hydrolysis equilibrium constant for several esters in an effort to determine if these constants have any relationship to the ionization constants of the corresponding acids. The hydrolysis equilibrium constants were directly determinable in only a very limited number of cases. Hydrolysis of propyl and isopropyl bromides and iodides in boiling alcohol containing small amounts of water, has been examined by Nicolet and Stevens.[36] It was found that these reactions are strongly catalyzed by the corresponding mercuric halides. In an attempt to determine the exact effect of diffused daylight on the rate of saponification of ethyl acetate by barium hydroxide in aqueous solutions, Gooch [37] made a number of observations which led him to believe that no such effect existed. Of general interest is a review of the history and development of the hydrolysis of benzene halides, prepared by Hale and Britton.[38] These authors described the commercial preparation of phenol from these compounds. Miller and Bandemer [39] have shown that acids adsorbed on ash-free charcoals are unable to invert sucrose. They suggest that adsorbed acids are in an undissociated state. According to these investigators the adsorption of acids does not necessarily imply a high concentration of hydrogen ions immediately surrounding the adsorbent. Kautz and Robinson [40] studied the rate of inversion of sucrose by $0.1N$ HCl in the presence of various alkali and alkaline earth chlorides. The results indicate that there is a parallelism between the rate of inversion and the activity of the hydrogen ion.

[33] Terry and Stieglitz, *J. Am. Chem. Soc.*, **49**: 2216 (1927).
[34] Harned and Hawkins, *J. Am. Chem. Soc.*, **50**: 85 (1928).
[35] Williams, Gabriel and Andrews, *J. Am. Chem. Soc.*, **50**: 1267 (1928).
[36] Nicolet and Stevens, *J. Am. Chem. Soc.*, **50**: 135 (1928).
[37] Gooch, *J. Am. Chem. Soc.*, **49**: 2257 (1927).
[38] Hale and Britton, *Ind. Eng. Chem.*, **20**: 114 (1928).
[39] Miller and Bandemer, *J. Am. Chem. Soc.*, **49**: 1686 (1927).
[40] Kautz and Robinson, *J. Am. Chem. Soc.*, **50**: 1022 (1928).

Catalytic Decomposition. The catalytic decomposition of a variety of substances has occupied the attention of several investigators. Taylor and Pickett [41] studied the decomposition of hydrogen sulfide in contact with hot platinum wire. This paper should be of interest in any consideration of sulfur poisoning of catalysts. Two investigations have been reported involving the decomposition of hydrogen peroxide. In one by French [42] the action of the iodine ion on hydrogen peroxide was examined. Robertson [43] found that manganese salts promote the action of potassium dichromate in the decomposition of hydrogen peroxide. His experiments indicate two superimposed, first order reactions. Lewis [44] studied the catalytic decomposition of sodium hypochloride solutions, containing oxides and peroxides of cobalt, copper, and iron. His results support the observations made by earlier investigators.

Adkins and Perkins [45] have investigated the decomposition of methanol vapor when brought into contact with alumina. Up to 350° C. they were able to convert the methanol almost quantitatively into dimethyl ether. At higher temperatures various gaseous products were produced, such as methane, carbon dioxide and carbon monoxide. When zinc oxide was employed as a catalyst, practically no ether was formed. Above 350° C. methanol was decomposed, yielding products similar to alumina. Alvarado [46] studied the dehydration of ethanol vapor by alumina at various temperatures. It is his belief that the dehydration takes place in at least two steps; first, the production of ether, and second, a further dehydration to give ethylene. For a given catalyst, the relative proportions of ether and ethylene appear to be dependent upon temperature and time of contact. Åkerlöf [47] studied the decomposition of diacetone alcohol in aqueous solutions of alkali metal hydroxides. The velocity was found to be proportional to the activity of the hydroxides present. In a later paper Åkerlöf [48] has reported additional work involving diacetone alcohol. He employed sodium hydroxide as a catalyst in varying water mixtures of a number of different alcohols. The velocity in pure primary alcohols increases with increasing molecular weight of the solvent. The reaction velocity in the pure alcohols decreases with the in-

[41] Taylor and Pickett, *J. Phys. Chem.*, **31**: 1212 (1927).
[42] French, *J. Phys. Chem.*, **32**: 401 (1928).
[43] Robertson, *J. Am. Chem. Soc.*, **49**: 1630 (1927).
[44] Lewis, *J. Phys. Chem.*, **32**: 243 (1928).
[45] Adkins and Perkins, *J. Phys. Chem.*, **32**: 221 (1928).
[46] Alvarado, *J. Am. Chem. Soc.*, **50**: 790 (1928).
[47] Akerlöf, *J. Am. Chem. Soc.*, **49**: 2955 (1927).
[48] Akerlöf, *J. Am. Chem. Soc.*, **50**: 1272 (1928).

creasing number of hydroxyl groups in the alcohol. In some cases the reaction velocity was largely influenced by the presence of small amounts of water.

Hydrocarbon and Alcohol Syntheses. Because of the interest which has developed in the synthesis of hydrocarbons and organic compounds containing oxygen, as, for example, the alcohols, it has been deemed advisable to include the investigations reported in this field under a separate heading. Smith has presented three papers during the past year dealing with this subject matter. His first paper [49] is largely concerned with a discussion of the equilibrium conditions which prevail in the formation of hydrocarbons and alcohols from water-gas. He calls attention to the difficulty of making a direct determination of such equilibria, because of the large number of products which may be formed when carbon monoxide and hydrogen react. His calculations indicate that it should be possible to produce from water-gas at atmospheric pressure and $300°$ C., any of the paraffin hydrocarbons providing suitable catalysts are available. Although the lower alcohols cannot be formed under these conditions, the higher alcohols are theoretically possible in considerable amounts. Calculated equilibrium constants are given for the formation of methane, ethane, propane, benzene, methanol, ethanol, and propanol. In a second paper, Smith, with Hawk,[50] has presented the results of experiments involving the decomposition of methanol vapor in contact with a large variety of catalyst materials. Zinc oxide alone and zinc oxide admixed with various other oxides, such as chromic acid, uranium oxide, or vanadium oxide, appeared to be good catalysts for this reaction. Cadmium oxide, together with chromic acid, also gave good results. They found that the activity of zinc oxide catalysts was greatly influenced by the method of preparation. In a third paper, Smith, with Davis and Reynolds,[51] has considered the possibility of producing hydrocarbons higher than methane from water-gas. They report the results of experiments involving a variety of catalysts. These investigators believe that this method of making liquid fuel has very distinct commercial possibilities.

Two papers have been published by Lewis and Frölich, in which they report the results of an investigation of the catalytic

[49] Smith, *Ind. Eng. Chem.*, **19**: 801 (1927).
[50] Smith and Hawk, *J. Phys. Chem.*, **32**: 415 (1928).
[51] Smith, Davis and Reynolds, *Ind. Eng. Chem.*, **20**: 462 (1928).

synthesis of alcohols. The first paper [52] is primarily concerned with the synthesis of methanol and discusses the effect of pressure, temperature, gas flow and catalyst poisons on this particular synthesis. In a second paper [53] they present the results of experiments which have been made in an effort to produce higher alcohols by synthesis from water-gas. They investigated a number of metal and oxide catalysts. In all cases there was an appreciable amount of carbon monoxide lost because of the side reactions which occurred. The higher the temperature the greater was the tendency for such wasteful side reactions. Of more theoretical significance, and yet of considerable interest in a consideration of catalysts for alcohol synthesis from water-gas, is the work of Taylor and Kistiakowsky.[54] They have studied the adsorptions of hydrogen, carbon monoxide and carbon dioxide on zinc oxide, and on zinc oxide and chromium oxide mixtures, at 0 and 100° C. They found that the adsorptive capacity per unit weight was considerably greater than has been observed for most metal catalysts, the adsorptive capacity of the zinc oxide-chromium oxide mixture being greater than the zinc oxide alone. This observation is held to be in harmony with the greater activity of the zinc oxide admixed with chromium oxide when employed in methanol synthesis.

Hightower and White [55] studied the equilibrium involved in the synthesis of methane from carbon monoxide and hydrogen. Equilibrium constants determined experimentally were somewhat less than those which they had calculated. The authors consider this discrepancy due largely to the difficulty of excluding side reactions which inevitably occur when carbon monoxide and hydrogen react. Walker [56] reports an attempt to produce liquid oily products from ethylene by contacting this gas with a number of different catalyst materials. Many of these, such as silica, borax, and zinc oxide, were found to be inert up to 600° C. Iron polymerized ethylene at 360°, yielding a colorless oil.

Miscellaneous. Griffin [57] has measured the adsorption of ethylene and hydrogen on a copper catalyst poisoned with carbon monoxide. He found that carbon monoxide produced an increased adsorption at low pressures and a decreased adsorption at high pressures. Rea and Mullinix [58] studied the action of ethylene in

[52] Lewis and Frolich, *Ind. Eng. Chem.*, **20**: 285 (1928).
[53] Frolich and Lewis, *Ind. Eng. Chem.*, **20**: 354 (1928).
[54] Taylor and Kistiakowsky, *J. Am. Chem. Soc.*, **49**: 2468 (1927).
[55] Hightower and White, *Ind Eng. Chem.*, **20**: 10 (1927).
[56] Walker, *J. Phys. Chem.*, **31**: 961 (1927).
[57] Griffin, *J. Am. Chem. Soc.*, **49**: 2136 (1927).
[58] Rea and Mullinix, *J. Am. Chem. Soc.*, **49**: 2117 (1927).

the conversion of starch to sugar. They consider that the results obtained indicate that the ethylene has a certain catalytic action. The effect of salts of iron, copper, manganese and mercury on the aging of rubber has been discussed by Taylor and Jones.[59] A catalytic method of estimating carbon monoxide in air has been described by Katz and Frevert.[60] The method involves the use of "Hopcalite," which catalyzes the oxidation of CO in air. In a later paper [61] they have given a very complete description of the application of this same method to the ventilation of the Holland Tunnel.

Pease and Chesebro [62] have studied the equilibrium which exists when methane reacts with steam to yield carbon dioxide and hydrogen. Equilibrium was approached from both sides with the aid of a nickel catalyst supported on diatomite brick. They have calculated the constants for this reaction at 500, 600, and 700° C. From a consideration of the action of water and of carbon dioxide on tin, Eastman and Robinson [63] have calculated equilibrium constants for the water-gas reaction at 50° intervals between 650 and 900° C. Weston and Adkins [64] found that almost any sample of metallic copper or copper compound would catalyze the Ullman reaction, the yield depending upon the particular sample of copper compound employed. The yield was also dependent upon the kind and amount of solvent and the dryness of the reagents. Adkins, with Broderick,[65] has reported the results of a study involving the rate with which acetaldehyde reacts with ethyl, methyl, isopropyl, and n-butyl alcohols. They found that there was no very great difference in the reactivities of the four alcohols for acetal formation. Davis and Elderfield [66] have examined the possibility of synthesis of methylamine from ammonia and methanol, using thorium oxide as a catalyst. Under optimum conditions they were able to convert about one third of the methanol to methylamine by this operation.

[59] Taylor and Jones, *Ind. Eng. Chem.*, **20**: 132 (1928).
[60] Katz and Frevert, *Ind. Eng. Chem.*, **20**: 31 (1928).
[61] Katz and Frevert, *Ind. Eng. Chem.*, **20**: 564 (1928).
[62] Pease and Chesebro, *J. Am. Chem. Soc.*, **50**: 1464 (1928).
[63] Eastman and Robinson, *J. Am. Chem. Soc.*, **50**: 1106 (1928).
[64] Weston and Adkins, *J. Am. Chem. Soc.*, **50**: 859 (1928).
[65] Adkins and Broderick, *J. Am. Chem. Soc.*, **50**: 178 (1928).
[66] Davis and Elderfield, *J. Am. Chem. Soc.*, **50**: 1786 (1928).

Chapter VII.

Determination of Crystal Structure by X-rays.

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The Methods of Crystal Analysis. No important methods of studying the structure of crystals have been developed during the past year. Although a detailed experimental knowledge of the scattering powers of different atoms will greatly improve the methods of diffraction analysis, practically no new data have been accumulated either in America or abroad. An effort [12] has been made to learn more about the electron distributions within certain atoms from previous measurements of scattering. These results and the possibility of getting a valid picture of atomic structure from F-curve data have recently [23] been questioned. The conflict in the conclusions of these two investigations is the result of differ- ent ideas of the relationships existing between Compton-scattered X-rays and those scattered rays which produce diffraction effects.

One paper [9] dealing with crystal structure methods has been published. It describes, in simplified terms and with examples, the procedure for the analysis of spectral photographs which is in common use amongst many European investigators. Another [41] contains the characteristic criteria for all of the special cases of tetragonal space groups. This completes a tabulation of all of the distinguishing criteria for atomic positions having a symmetry less than cubic. A relation [13] has also been deduced between the position of a reflection upon an oscillation spectrum photograph and the time during which its plane is in position to reflect.

The Results of Crystal Analysis. Several papers deal with the structures of metals and alloys. One of the most interest- ing [31] describes diffraction measurements upon the alkali metals. From earlier experiments it had been concluded that although the pattern of potassium is excellent at liquid air temperature, it can-

not be obtained at room temperature. It has therefore been suggested that this metal loses its crystallinity before melting. The new investigation contradicts these earlier observations in finding satisfactory powder lines at room temperature from potassium, sodium and lithium. Neither the data from this paper nor those from another recent examination [a] of the alkali metals at low temperatures support the contention that potassium has tetragonal symmetry. Measurements [25] have been made upon alloys of cadmium with mercury. Atomic arrangements [7] have been deduced for two intermetallic compounds of copper—Cu_2Mg and $CuAl_2$. Chromium has the same structure [33] whether it is electrodeposited "bright" or "burnt." It is always body-centered cubic with a unit of the same size as that of the fused metal. Photographs [30] taken both above and below the transformation temperature of β-brass are those of a body-centered cubic structure. The spacing of the β-brass is a function of its zinc content. Some X-ray studies [32] are recorded on high speed steels.

The powder diffraction data from SnI_4 were not long ago considered to contradict a previous structure based on Laue photographs. During this year a note has appeared [5] which emphasizes the correctness of the earlier determination. Similar powder measurements on $LiCl.H_2O$ were thought to show that it has a cubic atomic arrangement. A recent analysis [16] of the reflections from single crystals proves that $LiCl.H_2O$ is actually tetragonal with an atomic arrangement that is not even pseudo-cubic. The type of atomic grouping [14] that prevails in $LiI.3H_2O$ has been found. Laue and spectral data [22] from mercurous and mercuric iodides result in structures identical with those previously found by several investigators. The tetragonal crystals [20] of $R_2CuCl_4.2H_2O$, where R is potassium, ammonium or rubidium, have arrangements in which half of the chlorine atoms are slightly different from the others in their relations to the remaining atoms in the crystal. A detailed examination [41] of the structure of $ZrSiO_4$ seems to show that the symmetry of its SiO_4 groups departs somewhat from that of a regular tetrahedron. The general marshalling of the atoms given by this determination agrees with two [b] other recently published studies, but the positions of the oxygen atoms are not quite the same. More accurate spacing measurements [13] have been made upon KH_2PO_4 and $NH_4H_2PO_4$. A determination of the

[a] Simon and Vohsen, *Naturwissenschaften*, 15: 398 (1927).
[b] Binks, *Mineralog. Mag.*, 21: 176 (1926); Vegard and Sollesnes, *Phil. Mag.*, 4: 985 (1927).

oxygen positions in the potassium salt indicates that its PO_4 group does not have the form of a regular tetrahedron. This is particularly interesting since the tetrahedral PO_4 groups in Ag_3PO_4 are necessarily regular.

A space group determination [8] leads to a new space group, $2Di—13$, for the orthorhombic alkali sulfates, K_2SO_4, Rb_2SO_4 and Cs_2SO_4. Several rhombohedral crystals exist which are closely allied to the cubic alkali chloroplatinates and chlorostannates, both in crystallographic characteristics and in chemical composition. The general type of atomic arrangement in one [39] of these, $K_2Sn(OH)_6$, proves to be a distortion of the familiar cubic structure.

The last few years have seen an increasing interest in the structures of organic crystals, and a growing attempt to apply to them the methods of complete structure analysis. This tendency is reflected in the greater number of such studies made this year by American workers.

Serious difficulties confront thoroughgoing investigations of organic crystals. The most important one is a consequence of the fact that all of their atoms are light. Since most of the electrons in these atoms are involved in chemical bonding and presumably in the production of Compton-scattering, it will be particularly difficult to ascertain their relative diffracting powers. Furthermore interatomic distances cannot be directly of aid because as yet practically nothing is known about them when the bonding between atoms is not ionic. It has been thought that a gradual but sound approach could be made to the structure of simple organic crystals through the study of ammonium salts having one or more hydrogen atoms replaced by organic radicals. The first three papers [40, 17, 18] of such a series have been published. They record determinations of atomic positions in the compounds $N(CH_3)_4X$ and NH_3CH_3X, where X is Cl, Br or I, and a study of the space group of $NH_3C_2H_5Br$ and $NH_3C_2H_5I$.

The positions [6] of the halogen atoms in the two cyclic halides, $C_6H_6Cl_6$ and $C_6H_6Br_6$, have been found from their Laue and spectral reflections. The size and shape of the unit cell of crystals [19] of acetonylpyrrole have also been established. The probable molecule, of composition $C_{28}H_{36}N_4$, does not possess elements of symmetry. Some further measurements [34] are recorded of the diffraction lines of cellulose fibers. The interpretation given to these cannot, however, be considered as satisfactory.

The question of whether the valences of the central carbon atom of pentaerythritol have a tetrahedral or a pyramidal arrangement is still being discussed. An American paper [15] appearing this year agrees with a Japanese publication [c] in finding that Laue photographs call for a symmetry less than that assigned by previous crystallographic description.

A series of interesting investigations treats of the X-ray diffraction patterns of several groups of related organic liquids.[d] Two diffraction rings have been found [36, 37, 26] from each of a number of normal fatty acids and alcohols. One is practically constant in position; the position of the other is a function of the number of carbon atoms in the molecular chain. Similar measurements [38] have been made from several side chain alcohols. The data thus accumulated are interpreted in terms of an hypothetical cybotactic state intermediate between the regular array of crystallinity and complete molecular disorder. The normal liquid paraffins [35] differ from the foregoing long chain carbon compounds in not giving diffractions which vary with the number of carbon atoms in the molecule. Whether or not these experimental results are adequately explained by cybotaxis, they provide a necessary step towards a better understanding of the liquid state.

Diffraction measurements [2] upon unstretched films of rubber latex show that the positions of its lines depend upon its purity, upon the presence of solvent and upon both its freshness and the manner of its aging. Similar observations have been recorded upon china wood oil treated in various ways. Two papers [10, 11] contain measurements of the positions of the powder lines from several compounds important in the study of Portland cement.

In addition to the foregoing accounts of new experiments, several review papers have appeared. Two [3, 4] deal with metals, the others [1, 21] are of a more general nature.

Several articles of a purely theoretical nature have been published. One [24] of these discusses relations that might exist between a model carbon atom and a diamond structure built from such atoms. Two papers [27, 28] on the structures of the ethane molecule and of solid ethane are based on ideas no longer commonly used. Apparently much more significant is a consideration [29] of the influence of the relative sizes of ions upon certain properties of the crystals in which they occur. The known irregularities in the

c Nitta, *Bull. Chem. Soc. Japan*, 1: 62 (1927).
d Sogani, *Indian J. Physics*, 1: 357; 2: 97 (1927).

measured interatomic distances and in the melting and boiling points of the alkali halides are pictured as arising from the varied interplay of the repulsive and attractive forces of the ions involved. A quantitative interpretation of these irregularities is based upon an approximate formulation of the applicable principles of wave mechanics.

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15. Hendricks, *Z. Krist.*, **66**: 131 (1927).
16. Hendricks, *Z. Krist.*, **66**: 297 (1928).
17. Hendricks, *Z. Krist.*, **67**: 106 (1928).
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37. Stewart and Morrow, *Phys. Rev.*, **30**: 232 (1927).
38. Stewart and Skinner, *Phys. Rev.*, **31**: 1 (1928).
39. Wyckoff, *Am. J. Sci.*, **15**: 297 (1928).
40. Wyckoff, *Z. Krist.*, **67**: 91 (1928).
41. Wyckoff and Hendricks, *Z. Krist.*, **66**: 73 (1927).

Chapter VIII.

Heavy Acids.

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The manufacture of the heavy acids, one of the oldest divisions of the chemical industry, is less subject to revolutionary changes than most of the other branches of chemical manufacture.

The heavy acids are essentially tonnage products sold at low prices and made in plants which represent heavy capital invest- ments. The consumers of heavy acids are spread over a wide territory and the ratio of freight rates to factory price of acid, when long hauls are involved, is usually sufficient to insure the local acid producer, with an out-of-date plant, against the com- petition of more modern but distant plants.

Basic process changes may be made promptly in a single plant, but it requires years for a new process to supplant an older method throughout the industry. An excellent example is the thirty years required for the displacement of the Leblanc soda process, involving the manufacture of sulfuric acid and the re- covery and sale of hydrochloric acid, by the ammonia soda and electrolytic cell methods.

It is not surprising that the year now under review has failed to show any pronounced changes in acid manufacturing processes. There are some advances to record, and some trends to analyze, but time will have to produce the proof of industrial value.

Sulfuric Acid. The total output of sulfuric acid in the United States, for the year ending December, 1927, was slightly less than in 1926, apparently because of a larger carry over of super- phosphate by the fertilizer industry from 1926 to 1927.

Pyrites, which had improved its position as a source of sulfur for sulfuric acid manufacture in 1926, lost ground in 1927, the consumption being 66,000 tons less for the year. As several new contact plants designed for sulfur were started up in 1927, it

would seem likely that contact acid from sulfur displaced a certain amount of chamber acid production from pyrites.

The output of domestic pyrites showed a substantial gain in 1927, while imports shrank considerably. The tonnages of domestic and imported pyrites are now close together, whereas a year ago importations were more than twice domestic production.

European manufacturers continue to display interest in natural sulfates (particularly gypsum) as substitutes for sulfur and pyrites in sulfuric acid manufacture. The Bayer factory at Leverkusen is said to have a yearly capacity of 40,000 tons H_2SO_4 from calcium sulfate, and to contemplate further extensions. Molitor [1] has described various methods of utilizing calcium sulfate as a source of H_2SO_4.

The burning of sulfur so that uniform percentages of sulfur dioxide are obtained is receiving attention. An interesting adaptation of the pressure atomizing fuel oil burner to the burning of sulfur has been successfully made and is being employed in contact plants. By using a definite pressure on the molten sulfur and a regulated air supply, also under pressure, more uniform gas is available and the percentage of SO_2 can also be held much higher than with the ordinary types of sulfur burner. Merriam [2] has described a method of improving combustion by periodically drawing off the solid impurities which collect in the melting vessels of sulfur burners.

In Europe there is an evident interest, judged by the patent literature, in methods of obtaining high concentrations of SO_2 from weak gases by absorption in suitable organic liquids and subsequent release by heating. Howard [3] has patented a method of increasing the SO_2 content of weak gases by introducing and burning in weak gases, a definite amount of sulfur vapor. The atomizing sulfur burner with its possibility of high concentrations suggests another way of securing the same result.

The removal of dust from pyrites burner gases by means of a special form of cyclone separator is being tried in several plants. The dust removal is apparently satisfactory for chamber operations but additional secondary apparatus is required for contact plants.

The use of vanadium catalysts for contact acid manufacture is

[1] Molitor, *Chem. Ztg.*, **51**: 329, 370 (1927).
[2] Merriam, U.S.P. 1657545 (Jan. 31, 1928).
[3] Howard, U.S.P. 1650358 (Nov. 22, 1927).

the subject of a brief survey by Nickell,[4] who makes the prophecy that "within the next decade platinum catalysts for sulfuric acid will be entirely abandoned." The patent situation on vanadium catalysts seems a little obscure at the present time.

de Blois [5] has reviewed the merits and operations of the chamber and contact systems in detail, and described the platinum mass contact plant at Sudbury, Ontario, utilizing waste gases from a nickel smelter.

Chamber plant operations and methods for obtaining maximum yields are discussed by Newell,[6] while Healy,[7] in a review of the heavy chemical industry, draws attention to the possibility of producing 66° Bé. sulfuric acid from the Glover towers of chamber systems. Sulfur burner gases have already been utilized in chamber acid plants as a source of heat for concentrating part of the make of chamber acid to 66° Bé. The Glover tower functions normally and produces 60° Bé. acid, the concentrator output being so adjusted that sufficient thermal units remain in the sulfur gases, passing from the concentrator, to furnish the heat requirements of the Glover tower.

Larison [8] describes an arrangement of tower units and a special distributor used jointly as a means for increasing the circulating load over Gay Lussac towers and reducing the nitre consumption.

Increasing use is being made of NH_3 as a source of oxides of nitrogen for chamber plants. Killeffer [9] and Spangler [10] both describe NH_3 oxidation units, and Spangler gives a series of cost figures showing pronounced savings as compared to nitrate of soda.

The economic development of the sulfuric acid industry is reviewed by Kreps [11] and emphasis is laid on the great increase in United States production since 1913 as compared to the rest of the world. Statistics collected by the U. S. Department of Commerce show the United States output of sulfuric acid as 50% of the world's total production.

Hydrochloric Acid. In a previous survey [12] reference was made to the decline in the production of hydrochloric acid from

4 Nickell, *Chem. Met. Eng.,* **35**: 153 (1928).
5 de Blois, *Chem. Ind.,* **46**: 257 (1927).
6 Newell, *Chem. Met. Eng.,* **34**: 607 (1927).
7 Healy, *Chem. Met. Eng.,* **35**: 361 (1928).
8 Larison, U.S.P. 1631139 (June 7, 1927); U.S.P. 1638042 (Aug. 9, 1927).
9 Killeffer, *Ind. Eng. Chem.,* **19**: 1153 (1927).
10 Spangler, *Chem. Met. Eng.,* **35**: 342 (1928).
11 Kreps, *Chem. Met. Eng.,* **34**: 361-3 (1927).
12 Annual Survey of American Chemistry, II: 98 (1927).

salt and sulfuric acid. The past year has shown no marked change, and production is still about 20% of the available plant capacity.

By-product hydrochloric acid from electrolytic caustic soda plants, and lack of demand for salt cake are the depressing factors, and the patent literature reveals little interest in improving the manufacture from salt.

The Mannheim mechanical salt cake furnace, its operation, yields, and necessary repairs are the subject of a paper by Böhm,[13] who emphasizes the difference between furnaces operating for bi-sulfate and salt cake.

Distillation of aqueous solutions of hydrochloric acid having a greater concentration than the constant boiling point acid is the subject of a patent by Drefahl.[14] Ricard and Guinot [15] have described a means of concentrating dilute hydrochloric acid solutions by the addition of sulfonic acids and subsequent distillation.

Various proposals which have been made for the employment of hydrochloric acid in the liberation of phosphoric acid from phosphate rock, have evidently not progressed beyond the laboratory stage, as there is no record of commercial use.

Nitric Acid. Reference was made in the discussion of sulfuric acid manufacture and processes to the growing use of NH_3 as a source of oxides of nitrogen. The substitution of NH_3 for $NaNO_3$ in HNO_3 manufacture has not made quite the same progress, although there has been an increase in NH_3 oxidation-HNO_3 plants in the past year.

Chilean producers of $NaNO_3$ have improved their position, the total exports for the year ending June 30th, 1928, being approximately 3,000,000 tons, as compared to 1,950,000 tons for the previous year and 2,700,000 tons for 1913, the last prewar year. Deliveries to the United States show gains approximating the gains in total shipments, the figures being 1,176,000 to June 30th, 1928, and 754,250 to June 30th, 1927. The requirements for nitric acid production are of course a fraction of the imports and import figures do not have any value in determining the consumption of $NaNO_3$ by nitric acid manufacturers.

The Chilean producers have made great improvements in their processes and equipment, and as one result, the Chilean Government has announced, after surveying present production costs,

[13] Böhm, *Chem. Ztg.*, **52**: 101 (1928).
[14] Drefahl, U.S.P. 1628829 (May 17, 1927).
[15] Ricard and Guinot, Canadian P. 272,356 (July 12, 1927).

that the export tax of $12.00 per ton will remain in force for the year ending June 30th, 1929.

The "Guggenheim" extraction process and the various mechanical handling adjuncts are described in detail by Holmsen [16] and an estimated production cost of $27.60 per ton finished $NaNO_3$ is given.

The technology of HNO_3 manufacture from $NaNO_3$ has not shown much change. Hough [17] suggests the preparation of HNO_3 from nitrates by exposing and heating a suitable mixture of nitrate and H_2SO_4 in film form on agitator disks.

The theory and practice of the production of HNO_3 by the oxidation of NH_3 is the subject of a paper by Taylor, [18] and the same subject is also discussed by Parsons. [19]

Experiments are reported with catalysts other than platinum but no practical application seems to have been made.

The development of special chrome nickel steels for ammonia oxidation equipment has made useful progress and probably as a result of plant experience, it has been suggested that shipment of HNO_3 could be made in chrome steel drums.

[16] Holmsen, *Tek. Tid. Uppl.*, **58**: 1, 9 (1928).
[17] Hough, U.S.P., 1649901 (Nov. 22, 1927).
[18] Taylor, *Ind. Eng. Chem.*, **19**: 1250 (1927).
[19] Parsons, *Ind. Eng. Chem.*, **19**: 789 (1927).

Chapter IX.

Analytical Chemistry of the Common Metals.

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The metals are considered, as far as practicable, according to their grouping in the periodic table.

Sodium. Barber and Kolthoff [1] have greatly improved the method suggested by Blanchetière [2] for the determination of small amounts of sodium by precipitation as $(UO_2)_3MgNa(C_2H_3O_2)_9$. $9H_2O$. They substituted zinc for magnesium, obtaining the salt $(UO_2)_3ZnNa(C_2H_3O_2)_9.6H_2O$ which gives much more uniform and accurate results. The reagent is a solution of uranyl and zinc acetates in dilute acetic acid, saturated with the triple salt, and not less than ten times the volume of this reagent must be added to the solution. The precipitate is washed with the reagent, then with alcohol saturated with the salt, finally with ether and dried in the air. It contains 1.495% of sodium. This reagent is almost specific for sodium. Potassium (in absence of sulfate) up to 50 mg. per cc., ammonium, barium, calcium and magnesium in large amounts do not interfere. Lithium and strontium are partially precipitated. Organic acids and phosphates cause trouble.

Potassium. Reed and Withrow [3] have suggested the use of zirconium sulfate (100 to 200 g. per liter) as a fairly delicate test for potassium, although not nearly as delicate as the cobaltinitrite test. The limit is about 0.5 mg. potassium in a total volume of 2 cc. or about 250 mg. per liter, half the volume being the reagent added. The presence of considerable sodium decreases the delicacy of the test somewhat, but the effect of other metals was, unfortunately, not investigated. The precipitate of double sulfate forms

[1] Barber and Kolthoff, *J. Am. Chem. Soc.*, **50**: 1625 (1928).
[2] Blanchetière, *Bull. soc. chim.*, (4) **33**: 807 (1923).
[3] Reed and Withrow, *J. Am. Chem. Soc.*, **50**: 1515 (1928).

very slowly in dilute solution and to obtain maximum sensitivity the solution must be cooled to 0°.

Copper. Bonner and Kaura [4] have devised a method for separating copper and cuprous oxide depending on the fact that the metal is very slowly soluble in 0.5 molar sodium cyanide, while the oxide dissolves rapidly. The sample is treated with this solution for two hours and filtered. The metal remains in the residue while the oxide is determined by destroying the cyanide with nitric acid and estimating the copper iodimetrically. Holland and Gilligan [5] describe a convenient apparatus for the electrodeposition of copper in the analysis of insecticides.

Magnesium and Calcium. In spite of the enormous amount of work which has been done on the errors involved in the determination of magnesium and phosphorus as magnesium pyrophosphate, and on the proper procedure to follow, there is still some uncertainty on a few points. The careful work of Epperson [6] shows that, for exact work, a double precipitation is necessary, the second under exactly defined conditions. A large excess of ammonium chloride or of ammonia, or the presence of potassium, sodium, or ammonium oxalate, gives high results for magnesium. The same effect is always produced by the addition of phosphate to ammoniacal solutions. A very large excess of ammonium phosphate gives low results. It is immaterial whether the precipitation is made in hot or cold solution. McNabb [7] has shown that the addition of ammonium acetate assists in obtaining a crystalline precipitate of magnesium ammonium phosphate in the Schmitz method of determining phosphorus but that equally accurate results may be obtained without it. In order to determine the effect of carbonaceous matter from the filter paper during the ignition of magnesium pyrophosphate, Jacob and Reynolds [8] ignited mixtures of the salt with an equal weight of carbon in an atmosphere of nitrogen. In one to three hours at 900-975° the loss of phosphorus was 0.2 to 0.6% of the total amount; in one hour at 1000°, 2.5%; at 1050°, 12.5%; and at 1100°, 32%. Although the loss at 900° is small, it is obviously desirable to burn off the carbon at a lower temperature before the final ignition. An improvement in the alkalimetric titration of magnesium in the presence of calcium

[4] Bonner and Kaura, *Ind. Eng. Chem.*, **19**: 1288 (1927).
[5] Holland and Gilligan, *Ind. Eng. Chem.*, **20**: 533 (1928).
[6] Epperson, *J. Am. Chem. Soc.*, **50**: 321 (1928).
[7] McNabb, *J. Am. Chem. Soc.*, **50**: 300 (1928).
[8] Jacob and Reynolds, *J. Assoc. Official Agr. Chem.*, **11**: 128 (1928).

has been made by Pierce, Setzer and Peter.[9] The carbonates are dissolved in standard acid, carbon dioxide boiled off, and the excess of acid titrated using bromthymolblue as indicator, thus finding the acid required for the combined carbonates. Standard alkali is then added until all the magnesium is precipitated as hydroxide, as shown by the brick-red color of trinitrobenzene as indicator. A blank test is run to find the volume of alkali needed to match this color. Ferric iron does not interfere unless so much ferric hydroxide is precipitated in the neutral solution as to mask the color of the indicator but aluminum interferes by forming aluminate.

Metallic calcium, dissolved in 30% sucrose solution, has been suggested by Shead [10] as a primary standard in alkalimetry. However, in view of the practical impossibility of obtaining it pure, it cannot be seriously considered. Willard and Young [11] describe a new volumetric method for calcium in which the oxalate is dissolved in hydrochloric acid and titrated hot by standard ceric sulfate. The yellow color of the ceric salt serves as an indicator or the potentiometric method can be used. If iodine chloride is added as a catalyst, the reaction goes at room temperature and methylene blue serves as an indicator, forming a transient, pink color at the end point. Mathers and Wilson [12] have modified slightly the usual qualitative procedure to eliminate interference of strontium in testing for calcium by treating the carbonate precipitate on the filter with normal surfuric acid and adding to the filtrate ammonia and oxalate to precipitate the calcium oxalate or alcohol to precipitate the sulfate. This avoids the supersaturated solution of strontium sulfate often obtained by the usual method. Corey and Rogers [13] accomplish the same purpose by waiting twenty minutes before filtering off the strontium sulfate and diluting the filtrate with three parts of water before testing for calcium.

The standard sucrose method for determining the caustic value of lime has been improved by Shaw, MacIntire and Underwood [14] by the use of accurate filtering and measuring apparatus so that more accurate results are obtained in less time. Shaw and MacIntire [15] have tested the modified sucrose and Scaife methods

[9] Pierce, Setzer and Peter, *Ind. Eng. Chem.*, **20**: 436 (1928).
[10] Shead, *J. Am. Chem. Soc.*, **50**: 415 (1928).
[11] Willard and Young, *J. Am. Chem. Soc.*, **50**: 1322 (1928).
[12] Mathers and Wilson, *J. Chem. Education*, **4**: 1424 (1927).
[13] Corey and Rogers, *J. Chem. Education*, **4**: 1428 (1927).
[14] Shaw, MacIntire and Underwood, *Ind Eng. Chem.*, **20**: 312 (1928).
[15] Shaw and MacIntire, *Ind. Eng. Chem.*, **20**: 315 (1928).

in the presence of added magnesium oxide, which was without effect in the sucrose method; calcium aluminate, which increased the causticity; calcium silicate, calcined silica gel and aluminum oxide, which decreased it.

Zinc. The use of diphenylamine as indicator in the ferro-cyanide titration of zinc suggested by Cone and Cady [16] has been made the basis of a qualitative test by the same authors.[17] To the acetic acid solution containing the reagent, potassium ferricyanide is added and a dark brown, green or purplish black turbidity in-dicates the presence of zinc, the amount of which may be esti-mated by the depth of color produced.

Mercury. The method proposed by Booth, Schreiber and Zwick [18] for the determination of mercury in clinical material has been applied by Schreiber, Sollmann and Booth [19] to urine and feces and found to give excellent results, even in the presence of certain drugs, whereas other drugs interfere.

Aluminum. The method of testing for aluminum by means of alizarin S, described by Atack,[20] has been modified by Allar-dyce.[21] who adds to the suspension of aluminum hydroxide a solu-tion of alizarin in concentrated acetic acid which imparts a pink color to the precipitate. A detailed study of the colorimetric deter-mination of aluminum by the use of aurintricarboxylic acid and sodium alizarin monosulfonate (Atack's reagent) has been made by Yoe and Hill.[22] They show the effect of varying time, tem-perature, concentrations of reagents and of the presence of other ions and give a procedure which may be used for the determination of aluminum in water. Iron, nickel, cobalt, chromium and man-ganese interfere in both methods, silica and phosphate only when aurintricarboxylic acid is used.

Lead. To prevent the precipitation of stannic acid in the de-termination of lead in manganese bronze, Diana [23] dissolves it in nitric acid containing a large amount of ferric nitrate. From this clear solution the lead is deposited electrolytically as dioxide.

Arsenic. In the Gutzeit method for arsenic Heidenhain [24] finds that to obtain uniform stains it is important to regulate the

[16] Cone and Cady, *J. Am. Chem. Soc.*, **49**: 356 (1927).
[17] Cone and Cady, *J. Am. Chem. Soc.*, **49**: 2214 (1927).
[18] Booth, Schreiber and Zwick, *J. Am. Chem. Soc.*, **47**: 2625 (1925); **48**: 1815 (1926).
[19] Schreiber, Sollmann and Booth, *J. Am. Chem. Soc.*, **50**: 1620 (1928).
[20] Atack, *J. Soc. Chem. Ind.*, **34**: 936 (1915).
[21] Allardyce, *J. Am. Chem. Soc.*, **49**: 1991 (1927).
[22] Yoe and Hill, *J. Am. Chem. Soc.*, **49**: 2395 (1927); **50**: 748 (1928).
[23] Diana, *Chem. Analyst*, no. **47**: 6 (1927).
[24] Heidenhain, *J. Assoc. Official Agr. Chem.*, **11**: 107 (1928).

temperature of the generator and absorber. McCay [25] describes a new separation of arsenic from antimony. In a faintly ammoniacal solution containing the elements entirely in the pentavalent form, and containing considerable ammonium fluoride, silver nitrate precipitates silver arsenate quantitatively, free from antimony. The precipitate is dissolved in nitric acid and the silver titrated with thiocyanate. The fluoride solution is evaporated with sulfuric acid to fumes, the antimony reduced by boiling with sulfur and titrated in hydrochloric acid solution with bromate or permanganate. A silica dish is practically unattacked and pyrex may be used for the precipitation of silver arsenate. Willard and Young [26] have shown that arsenious acid may be titrated in hydrochloric acid solution with ceric sulfate using as a catalyst hydrobromic acid or iodine chloride, preferably the latter. Methylene blue may be used as the indicator or the end point may be determined electrometrically. Slightly more than the theoretical amount of ceric sulfate is used but the ratio is always constant.

Antimony. Antimony may be determined according to Willard and Young [26] by reducing the hydrochloric acid solution with sulfur dioxide and titrating with ceric sulfate using iodine chloride as a catalyst, as in the determination of arsenic.

Manganese. Stout and Whitaker [27] have modified the standard persulfate-arsenite method for manganese in steel by titrating the permanganic acid with vanadyl sulfate instead of arsenite, the manganese being reduced to a manganous salt. The authors claim as an advantage of the method the greater stability of vanadyl sulfate. This is not true if the arsenite is prepared in the proper way and the solution made neutral. Such a solution will keep unchanged for months.

Nickel. To avoid contamination of nickel alpha-benzil dioxime by chromium when it is precipitated from solutions containing the latter, Germuth [28] recommends the addition of tartrate and a little copper salt.

Cobalt. Clennell [29] has investigated the effect of other metals and the amount of reagent needed in the nitroso-β-naphthol method for cobalt.

Iron. Willard and Young [30] describe a method for the deter-

[25] McCay, *J. Am. Chem. Soc.*, **50**: 368 (1928).
[26] Willard and Young, *J. Am. Chem. Soc.*, **50**: 1372 (1928).
[27] Stout and Whitaker, *Ind. Eng. Chem.*, **20**: 210 (1928).
[28] Germuth, *Chem. Analyst*, 17, no 2: 3 (1928).
[29] Clennell, *Mining Mag.*, **36**: 270 (1927).
[30] Willard and Young, *J. Am. Chem. Soc.*, **50**: 1334 (1928).

mination of iron in ores by reducing in the usual way with stan-
nous chloride, zinc or aluminum and titrating the ferrous salt with
ceric sulfate, using diphenylamine as an indicator, or electro-
metrically. The end point is much sharper than when dichromate is
used. Arsenic does not interfere. Furman [31] also describes some
experiments on the electrometric titration. Because ferrous salts
in fairly concentrated hydrochloric acid are rapidly oxidized in the
air, Heisig [32] eliminates this error in the iodate titration of ferrous
salts by adding iodine chloride first, then hydrochloric acid and
finally the iodate. A number of organic compounds, such as form-
aldehyde and tartaric acid, may be present. In the determination
of ferrous iron in silicates Soule [33] dissolves the silicate in dilute
hydrofluoric and sulfuric acids in a pyrex flask, adds boric acid
and titrates with permanganate, applying a blank correction for
the glass dissolved, usually about one gram. This blank must be
determined by running a material of known ferrous content.
Brallier [34] has modified the usual method of titrating ferric iron
and chlorate with titanous chloride so as to avoid the necessity
of storing the latter in an inert atmosphere. Excess of reagent
is added and titrated back with ferric alum. The same volume of
reagent is immediately titrated in the same way. Ferrous iron is
oxidized by a slight excess of permanganate and the latter removed
by arsenite which does not interfere. An excellent method for the
colorimetric determination of iron is described by Lyons.[35] Thio-
glycolic acid reduces a ferric to ferrous salt and the latter in
ammoniacal solution forms an intense reddish purple color with
the excess of reagent. It gives a more intense color than thio-
cyanate, is independent of the state of oxidation and is capable of
detecting iron in a dilution of 1 : 10,000,000. Patten and Winter [36]
have made a further study of the method of Patten [37] for sep-
arating iron and aluminum from calcium in the presence of excess
phosphate and have developed a micro modification using colori-
metric methods for both metals. They have shown that the
phosphates of iron and aluminum are completely precipitated, even
at a pH of 4.3, but calcium phosphate not until 6.5 is reached.
Ammonium acetate is a suitable buffer. The results for iron are

[31] Furman, *J. Am. Chem. Soc.*, **50**: 755 (1928).
[32] Heisig, *J. Am. Chem. Soc.*, **50**: 1687 (1928).
[33] Soule, *J. Am. Chem. Soc.*, **50**: 1691 (1928).
[34] Brallier, *Ind. Eng. Chem.*, **19**: 846 (1927).
[35] Lyons, *J. Am. Chem. Soc.*, **49**: 1916 (1927).
[36] Patten and Winter, *J. Assoc. Official Agr. Chem.*, **11**: 202 (1928).
[37] Patten, *J. Assoc. Official Agr. Chem.*, **6**: 418 (1923).

slightly high but when both metals are present this practically compensates the loss due to solubility in the hot 5% ammonium nitrate wash solution. The determination of slag and oxides in wrought iron by a modified iodine method is described by Wescott, Eckert and Einert.[38] The iron is treated with iodine and water and the residue washed with water and 10% potassium hydroxide. It is ignited and weighed as oxide plus slag.

[38] Wescott, Eckert and Einert, *Ind. Eng. Chem.*, **19**: 1285 (1927).

Chapter X.

The Inorganic and Analytical Chemistry of Silver, Gold and the Platinum Metals.*

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The volume of work on the precious metals published by in vestigators in the United States during the past year was apparently somewhat greater than during 1925-26 or 1926-27. Possibly the event of greatest interest during the year was the symposium on precious metals held by the Institute of Metals at the winter meeting of the American Institute of Mining and Metallurgical Engineers. This symposium brought out several contributions from laboratories which are commercially interested in the manufacture or use of precious metals and their alloys. Among them was a paper by Kingsbury[1] on the behavior of a number of precious metals and alloys when used as contacts in electrical cir cuits, and one by Williams[2] on the metallurgical properties of precious metal alloys which affect their use in dentistry. Other papers presented at this symposium but dealing more specifically with gold, silver or the platinum group will be reviewed under the headings dealing with these metals.

A new Stamping Law for platinum metal alloys has been enacted in New York, New Jersey and Illinois. Although a National Stamping Law has not yet been enacted this will prob ably occur and meanwhile the state laws already in force apply to the sections of the country in which most of the platinum jewelry is manufactured. The legal situation, adequate manufac turing control and the scientific interest of the subject, all demand analytical methods which are more simple, more rapid and, above

all, more accurate and dependable than those now available. This is a good field for first class analytical research.

Silver. A number of papers appeared dealing with the properties of silver halides in photographic emulsions. Sheppard and Hudson [3] prepared the 1:1 addition compounds of allylthiourea with silver chloride, bromide and iodide. The solubilities in water of these compounds were determined over the range 15 to 50°. The paper discusses the constitution of the compounds and their relation to photographic sensitizing, earlier work [4] having shown that the photographic activity of certain gelatins depends upon the presence of allylthiourea and related substances.

The same authors [5] discuss the complex compounds of silver halides with thioanilides. They found that these compounds do not act as photographic sensitizers as they should if sensitizing is brought about merely by the introduction into the silver halide grains of a substance which readily absorbs or "accepts" halogens. They conclude that the union in the complex compound is through the nitrogen atom rather than the sulfur atom, and show that silver sulfide is not readily formed by decomposition of the complex compound. They regard the results as confirming the view [6] that silver sulfide is the effective agent when sulfur-containing sensitizers are used. In an earlier paper Sheppard, Trivelli and Wightman [7] offered evidence to show that the action of allylthiourea is to form specks of silver sulfide in the surface of the silver halide grains in a photographic emulsion.

Lambert and Wightman [8] studied the thermodynamics of several series of reactions which might provide the mechanism for Hickman's hypothesis [9] that silver sulfide acts as a "halogen acceptor" in sensitizing photographic emulsions. They conclude that this theory of the effect of silver sulfide is thermodynamically possible but do not accept the two alternative series of reactions suggested by Hickman.

Trivelli [10] offers a hypothesis as to the mechanism of the production of the latent image from sensitivity specks on the basis that these specks contain some silver as well as silver sulfide. He regards these specks as photoelectric cells in which silver is

[3] Sheppard and Hudson, *J. Am. Chem. Soc.*, **49:** 1814 (1927).
[4] Sheppard, *Phot. J.*, **65:** 380 (1925).
[5] Sheppard and Hudson, *Phot. J.*, **67:** 359 (1927).
[6] Sheppard, Colloid Symposium Monographs, 3: 76 (1925); *Phot. J.*, **65:** 380 (1925).
[7] Sheppard, Trivelli and Wightman, *Phot. J.*, **67:** 281 (1927).
[8] Lambert and Wightman, *J. Phys. Chem.*, **31:** 1249 (1927).
[9] Hickman, *Phot. J.*, **67:** 34 (1927).
[10] Trivelli, *J. Franklin Inst.*, **204:** 649 (1927); **205:** 111 (1928).

the cathode, silver sulfide the anode and silver bromide the solid electrolyte.

In a paper describing certain elaborations of the moving boundary method for determining transference numbers, MacInnes, Cowperthwaite and Huang [11] reported the cation transference number of 0.05 N silver nitrate solution to be 0.4664 at 25°, somewhat lower than previously published values. From evidence offered by transference and conductance measurements MacInnes and Cowperthwaite [12] believe that silver nitrate is not completely dissociated in solution. This is considered to be true for sodium nitrate and potassium nitrate also, in contrast to nitric acid and ammonium nitrate.

Sunier and Hess [13] determined the solubility of silver in mercury at temperatures from 80 to 200°, obtaining values ranging from about 0.3 atomic % at the lower temperature to about 1.7 atomic % at 200°. The paper includes a description of the methods used in preparing and analyzing the amalgams.

Randall and Young [14] described the conditions for the preparation of reproducible silver-silver chloride electrodes and made new determinations of the potential of the hydrogen silver-silver chloride cell, arriving at a value for the standard potential of 0.2221 volt at 25°.

Bush [15] investigated the supposed effect of exposing bichromate solutions to sunlight on the color of silver chromate subsequently precipitated from such solutions. It was found that this exposure to light was without effect but that differences in color of precipitated silver chromate were caused by varying the rate at which the reacting solutions were mixed.

The use of the exothermic reaction $3Ag_2S + 6NaOH = 6Ag + 2Na_2S + Na_2SO_3 + 3H_2O$ was proposed by Kirsebom [16] for the reduction of silver sulfide obtained in the extraction of silver from ores by precipitating cyanide solutions with sodium sulfide. Suggested methods of operation and estimates of costs are given.

A paper by Leach and Chatfield [17] describes the manufacture of sterling silver and gives data on some of the physical properties of this alloy.

[11] MacInnes, Cowperthwaite and Huang, *J. Am. Chem. Soc.*, **49**: 1710 (1927).
[12] MacInnes and Cowperthwaite, *Trans. Faraday Soc.*, **23**: 400 (1927).
[13] Sunier and Hess, *J. Am. Chem. Soc.*, **50**: 662 (1928).
[14] Randall and Young, *J. Am. Chem. Soc.*, **50**: 989 (1928).
[15] Bush, *J. Phys. Chem.*, **31**: 931 (1927).
[16] Kirsebom, *Eng. Mining J.*, **124**: 815 (1927).
[17] Leach and Chatfield, *Am. Inst. Mining Met. Eng.*, Tech Pub. no. 60 (1927). 13 p.

The work of Jordan, Grenell and Herschman on tarnish resisting silver alloys, abstracted in Volume II of this Survey, was published in greater detail during the current year.[18]

Gold. The potential of the gold-auric oxide electrode was determined independently by Gerke and Rourke [19] and by Buehrer and Roseveare.[20] The former investigators measured the potential of gold-auric oxide against mercurous sulfate-mercury and from existing data for the potential of the latter electrode calculated the potential of the gold-auric oxide electrode as 1.362 ± 0.002 volt at 25°. They computed the free energy of formation of auric oxide as $+ 18,810$ cal. and the dissociation pressure as 1.46×10^9 atmospheres, both at 25°. Buehrer and Roseveare measured the potential directly against the hydrogen electrode and obtained the value 1.364 ± 0.001 volt at 25°. They computed the value of $+ 19,100$ cal. for the free energy of formation of auric oxide and 2.13×10^9 atmospheres for the dissociation pressure, at 25°. Both groups of workers failed in attempts to prepare aurous oxide and hence to study the gold-aurous oxide electrode.[21]

Gilchrist [22] published the results of a series of tests to determine the accuracy which could be attained in the assay of gold alloys affixed to base metal alloys, as in filled gold and rolled gold plate. He used 10K yellow gold plate and 14K white gold plate in the experimental work. The effect of various stripping solutions and of other factors, such as the thickness of the layer of gold alloy, are discussed.

Gross and Scott [23] published an exhaustive paper on the use of charcoal in the recovery of gold and silver from cyanide solutions.

The specific gravity, Brinnell hardness, tensile strength, Erichsen ductility number, melting points, electrical resistivity, and thermal E.M.F. against platinum at 800°, of each of fifteen 14K and fifteen 18K gold alloys were determined by Carter.[24] The two series studied were ternary alloys with silver and copper, the two ends of each series containing 0% of silver and copper respectively.

Platinum Metals. Howe [25] published a more detailed paper, confirming the preliminary notice [26] which was reviewed in this

[18] Jordan, Grenell and Herschman, Bur. Standards, *Tech. Papers*, 21: 459 (No. 348).
[19] Gerke and Rourke, *J. Am. Chem. Soc.*, 49: 1855 (1927).
[20] Buehrer and Roseveare, *J. Am. Chem. Soc.*, 49: 1989 (1927).
[21] *Cf.* Buehrer, Wartman and Nugent, *J. Am. Chem. Soc.*, 49: 1271 (1927).
[22] Gilchrist, *Ind. Eng. Chem.*, 19: 827 (1927).
[23] Gross and Scott, Bur. Mines, Tech. Paper no. 378 (1927).
[24] Carter, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 86 (1928). 17 p.
[25] Howe, *J. Am. Chem. Soc.*, 49: 2381 (1927).
[26] Howe, *Science*, 65: 503 (1927).

chapter last year, on the so-called isomeric chlorides of ruthenium. The paper includes observations to show that the well known blue solution contains divalent rather than univalent ruthenium. Opportunity is taken here to correct a typographical error in last year's review. The compound known as the aquo or beta salt is established by Howe as the true chlororuthenite (not chlororuthenate), or better pentachlororuthenite monohydrate.

Crowell and Yost [27] distilled ruthenium tetroxide into acidified iodide solution and showed that ruthenium in this reaction is reduced to the trivalent state. Other work in their paper confirms the conclusions reached by Howe.[25] Krauss [28] dissents from these views.

In another paper Howe [29] outlined an approximate method for the determination of ruthenium by absorbing ruthenium tetroxide in hydrochloric acid, reducing this solution, supposedly of quadrivalent ruthenium, to the trivalent stage with an excess of stannous chloride and titrating back with iodine solution. The results of his experiments were always somewhat low, indicating the probability that some of the ruthenium tetroxide is reduced to the trivalent stage when absorbed in hydrochloric acid.

Yost and White [30] obtained a value of 12.3 for the distribution ratio (CCl_4/H_2O) of osmium tetroxide between carbon tetrachloride and water, at 25°, on the basis of volume concentrations. When dilute sodium hydroxide solutions (0.06 N and 0.03 N, approximately) were used instead of water the distribution ratio fell off to 2.2 and 3.8 respectively. From this they conclude that osmium tetroxide is the anhydride of the acid H_2OsO_5, which they propose to call perperosmic acid. The ionization constant of the first hydrogen of the acid is calculated to be 8.0×10^{-13} at 25°.

Based on a study of analyses of meteorites and other data, Howe [31] published an estimate of the relative amounts of the platinum metals in the earth. The order of preponderance is given as platinum, iridium, osmium, rhodium, palladium and ruthenium.

Davis [32] discussed the theory and the technic of the glow test for the platinum metals. Experiments were made on the several factors which are involved in the test. He found that the method

[27] Crowell and Yost, *J. Am. Chem. Soc.*, **50**: 374 (1928).
[28] Krauss, *Z. angew. Chem.*, **41**: 413 (1928).
[29] Howe, *J. Am. Chem. Soc.*, **49**: 2393 (1927).
[30] Yost and White, *J. Am. Chem. Soc.*, **50**: 81 (1928).
[31] Howe, *Science*, **66**: 220 (1927).
[32] Davis, *J. Franklin Inst.*, **203**: 679 (1927).

described by Curtman and Rothberg [33] may be safely applied only if copper, silver, cobalt and nickel are absent. A modified procedure is given which makes the test more reliable.

The spark spectrographic lines of platinum shown by a series of seven silver-platinum alloys containing 0.01 to 5% of platinum were determined by de Laszlo,[34] in the range 2335 to 3923 Ångstrom units. This work is suggested as the basis for the rapid approximate determination of platinum in silver beads which are obtained by cupellation or which may be prepared by direct fusion on charcoal.

Carter [35] discussed the melting, working and the uses of the platinum metals and many of their alloys. The physical properties of the metals and some of the alloys are given and a number of new data published. The paper also has a section on gases in the platinum metals, as well as sections on metallography and spectrography.

A method for the refining of miscellaneous platinum scrap was described by Whiteley and Dietz.[36] The paper also contains a section on the melting and working of platinum, palladium and the usual alloys of these metals with iridium, rhodium and gold.

Wichers, Gilchrist and Swanger [37] described methods for the preparation of each of the six platinum metals in any desired degree of purity. The procedures are based in part on methods in common use but new information is given for several of the metals, notably platinum and rhodium. The new procedure suggested for platinum offers the advantage of an almost quantitative elimination of impurities in one step.

Detailed directions for the preparation of the platinic oxide catalyst used in organic reductions were published by Adams, Voorhees and Shriner.[38]

[33] Curtman and Rothberg, *J. Am. Chem. Soc.*, **33**: 718 (1911).
[34] de Laszlo, *Ind. Eng. Chem.*, **19**: 1366 (1927).
[35] Carter, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 70 (1928). 24 p.
[36] Whiteley and Dietz, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 84 (1928). 9 p.
[37] Wichers, Gilchrist and Swanger, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 87 (1928). 29 p.
[38] Adams, Voorhees and Shriner, *Org. Syntheses*, **8**: 92 (1928).

Chapter XI.

Inorganic and Analytical Chemistry of the Rare Metals.

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Probably the most important contribution in this field of activity during the past year is the long-awaited text and reference book by Noyes and Bray [1] on the qualitative analysis for the rare metals. Material for this publication has been in preparation for over twenty years. The text is invaluable to all workers in this branch of chemistry and the authors merit both the thanks and the congratulations of their fellow chemists.

Thornton [2] has prepared a valuable monograph on titanium with special reference to the analytical treatment of titaniferous substances. Thornton is well known as an authority on the chemistry of this metal and chemists will consult his book with confidence.

Cooper,[3] of the Kemet Laboratories of Cleveland, Ohio, has prepared a very readable pamphlet on beryllium, concerned chiefly with the metallurgy of that element.

In taking up research work on the individual elements, the general plan will be to follow the order of the periodic arrangement.

Thomas and Hochwalt [4] gave a demonstration, at the St. Louis meeting of the American Chemical Society, of the use of water solutions of oxygen-containing salts of the alkali metals as fire extinguishing agents. They state that potassium nitrate, chromate, chlorate, perchlorate and lactate are especially effective, the perchlorate being best of all; and that rubidium and caesium

[1] Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements." New York, Macmillan, 1927. 536 p.
[2] Thornton, "Titanium, With Special Reference to the Analysis of Titaniferous Substances." New York, Chemical Catalog Co., 1927. 262 p.
[3] Cooper, "Beryllium, the Light Metal of the Future." Cleveland, Ohio, Kemet Laboratories Co., Inc. 24 p.
[4] Thomas and Hochwalt, *Chem. Met. Eng.,* **35**: 298 (1928).

compounds are progressively better. This curious phenomenon, they state, seems to have no satisfactory scientific explanation, and is referred to as a catalytic process. The writer is glad to record this addition to the uses of the rare alkalies, but he has not the vision to see the day when these salts can be used for extinguishing fires of any considerable magnitude. It may also be of interest to note that the extinguishing value seems to increase with the insolubility of the salts.

Kolthoff [5] has shown that a 0.1% solution of curcumin in alcohol is adsorbed by beryllium hydroxide in a weakly alkaline solution, with the formation of an orange-red color. The sensitivity extends to 0.05 mg. of beryllium per liter. The presence of aluminum has a disturbing effect, but it can be removed by sodium fluoride, which precipitates the greater part of the aluminum as Na_3AlF_6.

Bergstrom [6] has prepared, by the action of a solution of the corresponding alkali metal, or alkali metal amide, upon metallic beryllium, potassium and sodium, ammono beryllates such as $Be(NH_2)NHK.NH_3$ and $Be(NH_2)NHNa.NH_3$. These salts resemble one another closely both in physical and in chemical properties.

The same investigator [7] has also studied the action of liquid ammonia solutions of ammonium salts on metallic beryllium, and by acting on the metal with liquid ammonia solutions of ammonium chloride and bromide has found normal halides with ammonia of crystallization. The salts formed were $BeCl_2.4NH_3$, $BeCl_2.2NH_3$ and $BeBr_2.4NH_3$. A series of ammonobasic halides were also formed and described. These salts were produced by acting upon metallic beryllium with solutions of the normal halides of beryllium in liquid ammonia. The salts formed were $3Be(NH_2)_2.BeI_2.4NH_3$ and $5Be(NH_2)_2.BeI_2.4NH_3$.

Papish and Holt [8] have applied the arc spectrographic method to the detection and estimation of gallium, and have examined fifty-five minerals. The limit of sensitivity was about 0.001%, the lines last to disappear being 2943.2 and 2874.2. By noting the relative strength of the ten lines from 4172.0 to 2338.6 some indication of the amount of gallium present may be determined. About 70% of the minerals examined showed the presence of gallium.

[5] Kolthoff, J. Am. Chem. Soc., **50**: 393 (1928).
[6] Bergstrom, J. Am. Chem. Soc., **50**: 652 (1928).
[7] Bergstrom, J. Am. Chem. Soc., **50**: 657 (1928).
[8] Papish and Holt, J. Phys. Chem., **32**: 142 (1928).

In the same paper a method for the extraction of gallium from lepidolite is described: The finely powdered mineral was fused with twice its weight of potassium hydroxide in a nickel crucible. The fused mass was placed in water in a tall glass cylinder and stirred by a current of air, and the water then removed. The residue, containing the gallium and aluminum, was dissolved in hydrochloric acid and evaporated to remove silica, and the aluminum and gallium then extracted by dilute hydrochloric acid. This solution was treated with ammonium acetate to neutralize the mineral acid, an excess of acetic acid added, and then potassium arsenite. After treatment with sulfur dioxide to make sure of the reduction of all arsenic to the arsenious condition, the galliferous arsenious sulfide was precipitated by hydrogen sulfide. This precipitate was decomposed by nitric acid, the solution evaporated with hydrochloric acid, the arsenic reduced by sulfur dioxide and removed from the gallium by hydrogen sulfide in hydrochloric acid solution. From the filtrate gallium was precipitated by potassium ferrocyanide. This is the method in outline; the original paper should be consulted for details. All the separations were checked up by the spectroscope. One kilogram of mineral yielded 0.0887 gm. of Ga_2O_3 or about 0.007%.

Brown, Brothers and Etzel [9] have studied the catalytic activity of thallium and found that thallium on asbestos retains its activity for a comparatively long time and is an excellent catalyst for the production of azobenzene. At 260° the best yield was obtained, namely 7.8% of aniline and 74.8% of azobenzene, a total of 82.6%. The rate of flow of nitrobenzene was 4 gm. per hour. The catalyst was prepared by reducing a mixture of aluminum and thallic hydroxides containing 60% of thallium, at 260° by hydrogen.

Baxter and Butler [10] have revised the atomic weight of titanium by the analysis of titanium tetrabromide and, taking into consideration their previous work on the tetrachloride of titanium, they agree on the value 47.9. Those of us who are familiar with Baxter's work will accept this as the last word on the subject.

Botts and Krauskopf,[11] after studying the electrochemistry of titanium, make the following observations: Single potential measurements of titanium were made in M/4 solutions of $TiCl_3$ and $Ti(SO_4)_2$. If the normal hydrogen electrode potential is consid-

[9] Brown, Brothers and Etzel, *J. Phys. Chem.*, **32**: 456 (1928).
[10] Baxter and Butler, *J. Am. Chem. Soc.*, **50**: 408 (1928).
[11] Botts and Krauskopf, *J. Phys. Chem.*, **31**: 1404 (1927).

ered as zero, positive titanium has an average potential in TiCl$_3$ solution of 0.23 and in Ti(SO$_4$)$_2$ solution of 0.18. The presence of a small amount of hydrofluoric acid increases the single potential 0.22 volt. Hydrochloric and sulfuric acids cause a decrease. . Alkali salts of a common ion with titanium cause a slight increase. Replacement reactions show a marked similarity to analogous reactions with elemental silicon.

Brallier [12] has made a study of the determination of chloric acid and iron by means of titanous chloride, and concludes that for all ordinary purposes the method is both rapid and sufficiently accurate.

There has been considerable activity on the part of Dennis and his associates at Cornell University this year in the study of germanium and its compounds.

Dennis and Laubengayer [13] have prepared germanium tetrafluoride by different methods, and conclude that the thermal decomposition of barium germanate is the most satisfactory. They purified the gas by fractional distillation at a low temperature. Some of the chemical and physical properties of the gas were ascertained.

Orndorff, Tabern and Dennis [14] prepared the triphenyl germanium halides, tetrabenzyl germanium, simple and substituted phenyl germanic acid anhydrides and tetra-*n*-butyl germanium.

Papish, Brewer and Holt [15] have studied the arc spectrum of germanium and applied it to the detection and estimation of germanium in certain tin minerals and in enargite. The enargite was decomposed by nitric acid, evaporated with sulfuric acid to remove oxides of nitrogen, and the residue was distilled with hydrochloric acid in the presence of chlorine. Germanium tetrachloride distills over.

Brewer and Dennis [16] have determined the vapor pressure of germanium bromide for the temperature range 0° to the boiling point. The boiling point was found to be 186.5°.

Tressler and Dennis [17] have prepared fused metallic germanium by reducing germanium dioxide with carbon under a flux of sodium chloride. The yield is about 90%.

Brewer and Dennis [18] have described the preparation of ger-

[12] Brallier, *Ind. Eng. Chem.*, **19**: 846 (1927).
[13] Dennis and Laubengayer, *Z. physik. Chem.*, **130**: 520 (1927).
[14] Orndorff, Tabern and Dennis, *J. Am. Soc.*, **49**: 2512 (1927).
[15] Papish, Brewer and Holt, *J. Am. Chem Soc.*, **49**: 3028 (1927).
[6] Brewer and Dennis, *J. Phys. Chem.*, **31**: 1101 (1927).
[i] Tressler and Dennis, *J. Phys. Chem.*, **31**: 1429 (1927).
[s] Brewer and Dennis, *J. Phys. Chem.*, **31**: 1526 (1927).

manium dibromide, bromoform and di-iodide. The dihalides are strong reducing agents, similar to the corresponding tin compounds. The bromoform is produced by the action of a halogen acid upon the corresponding dihalide of germanium.

Brewer [19] made a comparative study of the dihalides of germanium, tin and lead.

Dennis and Joseph [20] have studied the best conditions for the preparation of germanium monosulfide by passing a current of hydrogen sulfide over the heated disulfide. They found the optimum temperature to be about 480° C. The product is crystalline, hard, black, opaque, and practically insoluble in mineral acids.

Nickell [21] has discussed the advantage of complex vanadium silicate catalysts which have brought about a conversion of SO_2 to SO_3 amounting to 97% to 98%. They not only have the advantage over platinum of decreased cost but they are not subject to poisoning by arsenic and hydrochloric acid, which may be present. Nickell concluded his paper with the prediction that within the next decade platinum catalysts will be abandoned.

Marden and Rich [22] have studied the preparation of vanadium and concluded that the best method is the calcium-calcium chloride process which they had worked out in a previous investigation for the preparation of thorium powder. The equation representing the process is: $V_2O_5 + 5Ca + 5CaCl_2 = 2V + 5CaO \cdot CaCl_2$. They found that the metal resembles tantalum and not arsenic and bismuth as previously stated. It is not brittle, but may be cold-worked into wire or other forms.

Stout and Whitaker [23] have applied standard vanadyl sulfate solutions to the volumetric estimation of manganese in steel. This vanadate method eliminates troublesome filtrations or unstable standard solutions required by other methods.

Doerner [24] has given two methods for the extraction of molybdenum from ores. (1) The ore is treated with hot sodium carbonate solution, the solution is acidified with sulfuric acid and digested with lead sulfate in the presence of sodium acetate; this precipitates lead molybdate. (2) The ore is digested with warm dilute sulfuric acid and the solution neutralized with scrap iron. The molybdenum is precipitated as the hydrated molybdenum

[19] Brewer, *J. Phys. Chem.*, **31**: 1817 (1927).
[20] Dennis and Joseph, *J. Phys. Chem.*, **31**: 1716 (1927).
[21] Nickell, *Chem. Met. Eng.*, **35**: 153 (1928).
[22] Marden and Rich, *Ind. Eng. Chem.*, **19**: 786 (1927).
[23] Stout and Whitaker, *Ind. Eng. Chem.*, **20**: 210 (1928).
[24] Doerner, U. S. Bur. Mines, Tech. Paper 399 (1926).

dioxide. A practically complete separation of molybdenum is obtained by roasting the product with chlorine at 450°.

Papish and Hoag [25] detect uranium by a photo-luminescence test; using uranium as an activator upon sodium fluoride a vivid yellow luminescence is produced.

Bradt and Lyons [26] detect selenium in organic compounds by oxidizing the material in a Carius tube with nitric acid to selenious acid. The selenious acid is titrated with standard silver nitrate in neutral solution with the use of sodium chromate as an outside indicator. Halogens must be absent.

Wells [27] has tested sulfuric acid for selenium by distilling a 100 gm. portion placed in a 200 cc. retort with 0.5 to 1 gm. of potassium bromide dissolved in 3 to 4 cc. of bromine water. The distillate is brought in contact with 3 to 4 cc. of strong hydrochloric acid saturated with sulfur dioxide. The bromide of selenium distills over and the sulfur dioxide reduces it to red selenium. The distillation is continued until the distillate is colorless and then it is allowed to stand six hours.

Lenher and Fruehan [28] have prepared and analyzed ammonium seleno-tungstate, $(NH_4)_2WSe_4$, and ammonium diseleno-tungstate, $(NH_4)_2WSe_2O_2$ and studied their properties and crystal form.

As conclusion to this chapter, attention is called to a new trade journal, "Foote-Prints," published by the Foote Mineral Company of Philadelphia. In this journal, issued quarterly, may be found several pages of abstracts of current literature bearing upon the applications of the rare metals to industrial processes, and other items of interest having to do with this group of elements.

[25] Papish and Hoag, *Proc. Nat. Acad. Sci.*, **13**: 726 (1928).
[26] Bradt and Lyons, *Proc. Indiana Acad. Sci.*, **36**: 195 (1927).
[27] Wells, *J. Wash. Acad. Sci.*, **18**: 127 (1928).
[28] Lenher and Fruehan, *J. Am. Chem. Soc.*, **49**: 3076 (1927).

Chapter XII.

Aluminum.

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Production. The extraction of alumina from clay is still the subject of investigation. Tilley, Millar and Ralston [1] have reviewed the various proposals for the extraction of alumina by acid proc esses from such ores as clay, alunite, leucite, etc. The treatment of clay with sulfuric acid is considered in detail and several new methods are proposed for purification of the aluminum sulfate and its conversion to alumina. A method of heating in retorts with a carrier gas to remove oxides of sulfur allows more com plete decomposition at lower temperatures without the formation of cakes or accretions and with more efficient heat transfer. The gases can be converted to sulfuric acid for reuse. Aluminum sul fate may be decomposed on a down-draft sintering machine where acid recovery is unnecessary and produces an oxide containing about 0.75% sulfur as aluminum sulfate. Moldenke has patented a process of recovering alumina from alunite, which involves digestion with sulfuric acid and separation of the products. [2]

The present trend in the purification of alumina for use in the electrolytic reduction of aluminum appears to be towards the de velopment of electrothermal processes.

Shumaker has found the use of fluxing agents such as magnesia to be desirable in the electrothermal production of aluminum- copper alloys. [3]

Alloys. Dix and his co-workers have continued their investi gations of the equilibrium relations in aluminum alloy systems. In addition to the previously reported work on the systems aluminum-copper, aluminum-iron, and aluminum-manganese, Dix

[1] Tilley, Millar and Ralston, U. S. Bur. Mines, Bull. no. 267 (1927). 85 p.
[2] Moldenke, U.S.P. 1637451 (Aug. 2, 1927).
[3] Shumaker, U.S.P. 1644000 (Oct. 4, 1927).

and Heath have now published their observations on the systems aluminum-silicon and aluminum-iron-silicon.[4] The aluminum used in this investigation was made by the Hoopes electrolytic refining process and had a purity of 99.951%. The solid solution limits of silicon in aluminum, which are of great practical interest in connection with heat treatment processes, were determined to be as follows: 1.65% silicon at 577° C., the eutectic temperature; 0.80% silicon at 500° C.; 0.29% silicon at 400° C.; 0.05% silicon at 200° C. The results obtained at 200° C. are of considerable interest because other investigators have not concerned themselves with the solubility at this low temperature, presumably because of the long time required to reach equilibrium. The maximum annealing time used in determining the solubility at 200° C. was 3100 hours. Areas of alloys which were prepared to show a uniform eutectic structure were analyzed and showed a silicon content of 11.8% as compared with 11.6% found by Edwards, by thermal methods. The solidus curve was also located and is given in the equilibrium diagram published by Dix and Heath.

Iron and silicon occur in small quantities in all commercial aluminum and exert a profound influence on its properties. It is important, therefore, to have an exact knowledge of the relationship of silicon and iron in the ternary system with aluminum. Aluminum-iron-silicon alloys were prepared containing as high as 40% iron and 29% silicon. An alloy corresponding to the composition $FeAl_3$ was prepared and was found to be completely homogeneous, which seems to prove the existence of this compound. The eutectic of $FeAl_3$ with aluminum contains 1.7% iron and melts at 655° C. $FeAl_3$ is practically insoluble in aluminum. Dix and Heath have suggested that the constituent of commercial aluminum commonly known as "X" be designated as α-(Fe-Si) and the second alloy of aluminum-iron-silicon be known as β-(Fe-Si). The first of these constituents commonly occurs in the form of "Chinese script" crystals, while the latter is found as curved needles.

Archer, Kempf and Hobbs have investigated the heat treatment of aluminum-silicon alloys.[5] They found in general that short-time heat treatment at temperatures around 565° C., followed by quenching, favored the predominance of the solution effect, while a long-time treatment favored the spheroidizing of the silicon

⁴ Dix and Heath, *Am. Inst. Mining Met.*, Tech. Pub. no. 30 (1927), 31 p.
⁵ Archer, Kempf and Hobbs, *Am. Inst. Mining Met.*, Tech. Pub. no. 23 (1927).

particles. The strength and hardness of the castings may thus be increased by short heat treatments but reduced by long heat treatments. The plasticity of the aluminum-silicon alloy tends to be decreased by the short-time treatment, because of the solution effect, but is increased if the heat treatment is prolonged, because of the spheroidizing effect. Elongation is a complex property depending on both strength and plasticity. It may be increased by a solution heat treatment which at the same time decreases plasticity; it may be further increased when the spheroidizing effect increases plasticity and might ultimately be decreased by the loss of strength due to spheroidizing, although this stage was not reached in the authors' experimental work.

A high-resistance aluminum alloy containing manganese and zinc, and suitable for motor rotors, has been patented by Fuller.[6]

As a minor alloying element in steel, aluminum is receiving considerable attention, particularly in alloys of the "Nitralloy" type. Homberger and Zavarine have described the properties of some of these steels.[7] A low-temperature treatment with ammonia gas, of steels containing aluminum, along with chromium or chromium and nickel, produces an extremely hard surface without deformation of the material and without subsequent heat treatment.

Nagel [8] has given in considerable detail, a review of the various processes used in the commercial fabrication of aluminum and its alloys. Faragher [9] has similarly described the commercial forms and applications of aluminum and aluminum alloys.

Experiments dealing with the relation to the direction of rolling of the "stalk-like" (columnar) crystals in cast aluminum, copper and zinc, have been described by Seidl.[10] He concluded that the axis of the columnar crystals perpendicular to the rolling plane is the most unfavorable condition. A homogeneous, finely granulated cast structure is most desirable for rolling.

Corrosion. In a series of reports to the National Advisory Committee for Aeronautics, Rawdon has discussed the various phases of the problem of the corrosion embrittlement of duralumin.[11] The corrosion of heat-treated aluminum alloys by intergranular attack has assumed importance because of the use of

[6] Fuller, U.S.P. 1645099 (Oct. 11, 1927).
[7] Homberger and Zavarine, *Trans. Am. Soc. Steel Treating*, 13: 297 (1928).
[8] Nagel, *Am. Inst. Mining Met.*, Tech. Pub. no. 32 (1927).
[9] Faragher, *Am. Inst. Mining Met.*, Tech. Pub. no. 33 (1927).
[10] Seidl, *Mining Met.*, 8: 454 (1927).
[11] Rawdon, Nat. Advisory Comm. Aeronautics, *Tech. Notes* nos. 282, 283, 284, 285 (Apr., 1928).

these materials in aircraft construction. The importance of the heat treatment conditions, and in particular the necessity for quenching in cold water in order to decrease susceptibility to corrosion, are recognized. It is now quite possible to prevent such corrosion by the use of protective coatings. The most practical solution to the problem appears to lie in the duplex products consisting of a strong alloy core with a pure aluminum surface. "Alclad" sheet, made according to the process of Dix, is of this type and is coming into constantly increasing use as its virtues become better understood.[12]

The experiments of McAdam on the corrosion-fatigue of non-ferrous metals included a study of certain aluminum alloys and duralumin in particular.[13] The tests showed that corrosion-fatigue becomes quite noticeable in duralumin, especially at normal stresses above 25,000 lbs. per square inch. Heat treatment of duralumin appeared to have little effect on its corrosion-fatigue limits.

Taylor [14] investigated the corrosion resistance and physical properties of certain alloys of aluminum, zinc and tin. Cracking and swelling of aluminum-tin alloys was especially noticeable in sodium chloride solutions, while all of the ternary alloys swelled and cracked to some extent.

Miscellaneous. The commercial electroplating of aluminum has been none too well established, and the opinion has prevailed in many quarters that aluminum cannot be satisfactorily plated. The principal difficulty apparently has been in obtaining coatings which were adherent under service conditions. Work, who has been investigating this subject for the past two years at the Mellon Institute, has published a summary of the progress made in this investigation.[15] It appears entirely practical to electroplate aluminum, provided the surface is given the proper preliminary treatment. A suitable treatment consists of an etch with a solution of hydrochloric acid containing salts of nickel, iron or manganese. The composition of the etching solution is varied, depending on the composition of the aluminum or aluminum alloy to be treated. An important effect of the etch is to roughen the surface of the aluminum and to leave it covered with a series of undercut pits which provide an excellent anchorage for the succeeding electro-

[12] Dix, *Mining Met.*, **8**: 395 (1927).
[13] McAdam, *Am. Soc. Testing Materials*, Preprint 36 (1927).
[14] Taylor, *Am. Inst. Mining Met.*, Preprint 1632-E (1927).
[15] Work, *Am. Electrochem. Soc.*, Preprint 23 (Apr., 1928).

plate. The author has suggested detailed procedures for plating aluminum and its commonly used wrought and cast alloys.

The aluminum electrolytic condenser is receiving greater attention as a result of careful scientific studies of its characteristics and performance. Siegmund [16] has published many interesting results secured in the course of an extended investigation of the aluminum electrolytic condenser in the Bell Telephone Laboratories. He has found that, in general, the higher the purity of the aluminum, the more rapid is the film formation and the lower is the resulting leakage current; the purest aluminum tested did not always show the greatest freedom from corrosion difficulties. Cells that have been operated for 6 or 7 years indicate an extended life for this type of condenser, when properly constructed.

The aluminum electrolytic rectifier has enjoyed a considerable vogue as a current rectifier for charging small storage batteries and as a rectifying element for plate current supply in radio receivers. Holland [17] has described the principal details of successful units of this character. Grimditch and Hunsberger [18] have found that for the successful functioning of the aluminum electrode, it should contain at least 0.04% copper. An electrode with a lower copper content than this delivers a greatly reduced current and shows unsatisfactory life; practical limits are 0.05 to 0.15% copper. A satisfactory electrolyte contains dibasic ammonium phosphate, potassium phosphate, and malic or citric acid; ferrosilicon makes a satisfactory companion electrode for the aluminum. Aluminum has also been used in the dry type of current rectifying device by Ruben.[19]

Aluminum screw threads have a tendency to seize when under considerable pressure, and Taylor has found that this seizing tendency can be eliminated by giving the contacting surfaces a coating of aluminum oxide.[20] Pacz [21] has patented another process for coating aluminum by immersion, which employs a solution containing sodium fluosilicate and nickel or cobalt sulfate, nitrate or chloride and sodium, potassium or ammonium nitrate. Downs has proposed the use of grained aluminum as a carrier for catalysts, particularly vanadium oxide.[22]

[16] Siegmund, *Am. Electrochem. Soc.*, Preprint 14 (Apr., 1928).
[17] Holland, *Am. Electrochem. Soc.*, Preprint 28 (Apr., 1928).
[18] Grimditch and Hunsberger, U.S.P. 1662383 (Mar. 13, 1928).
[19] Ruben, U.S.P. 1649741-1649743 (Nov. 15, 1927).
[20] Taylor, U.S.P. 1661448 (Mar. 6, 1928).
[21] Pacz, U.S.P. 1638273 (Aug. 9, 1927).
[22] Downs, U.S.P. 1672308 (June 5, 1928).

The Bureau of Standards has performed a service for all interested in aluminum by publishing a new and up-to-date edition of its Circular on light metals and alloys.[23] This edition was compiled by Miss M. G. Lorentz with the aid of the Bureau staff.

[23] U.S. Bur. Standards, Circ. no. 346 (1927).

Chapter XIII.

Chromium Group Metals.

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Of the four metals of this group, chromium, molybdenum, tungsten and uranium, most of the American publications during the period July 1, 1927, to July 1, 1928, were concerned with the chemistry, metallurgy and physics of chromium. Next in impor- tance was tungsten due primarily to its increasing use for purposes other than for high speed steel alloys.

Physical and Chemical Studies. The atomic weight as ac- cepted for 1928 to 1930[1] is 52.01 for chromium whereas for tungsten and molybdenum the round figures 184 and 96 are re- tained. The value 184 was determined by Edgar F. Smith, whose death early in 1928 marked the passing away of one of the fore- most chemists of America. Smith's chemistry of tungsten forms the basis of the processes universally applied to the commercial production of pure tungsten metal for incandescent lamps, radio tubes, X-ray tubes, contacts, etc.

The phosphorescence of calcium tungstate induced by X-rays was investigated by Swindells.[2] The rate of decay of a very phosphorescent sample of $CaWO_4$ was determined photographi- cally and found to fit the empirical equation of Becquerel: $I^{-x} = a + bt$, within the experimental error, from 30 seconds to five minutes after the exposure to X-rays. The intensity of phos- phorescence was found to be closely proportional to the product of the intensity of the X-rays and the time of exposure up to a limiting value, beyond which increased exposure caused a neg- ligible increase in the phosphorescence. For $CaWO_4$ fluorescence is an entirely distinct process. Taking two samples of the tungstate

[1] Baxter, *J. Am. Chem. Soc.,* **50**: 603 (1928).
[2] Swindells, *J. Optical Soc. Am.,* **16**: 165 (1928).

showing widely different ability to phosphoresce, Swindells found they had practically the same fluorescence. The fluorescence may be due to the presence of some unknown impurity in the tungstate.

Davisson and Germer [3] published a note on the thermionic work function of tungsten. Evidence was obtained that conductive electrons within the tungsten filament do not possess normal thermal energies. New calculations were submitted by Jones, Langmuir, and Mackay [4] for the rates of evaporation and the vapor pressures of tungsten, molybdenum, platinum and a number of other metals. On the basis of the new temperature scale of Forsythe and Worthing [5] older values were recalculated and it was found that the experimental data check the third law of thermodynamics as shown by the constancy of the calculated value for λ_0, the latent heat of evaporation at the absolute zero. The values of λ_0 expressed in cal. gm. $(atom)^{-1}$ and the boiling points in degrees Kelvin are:

	W	Mo	Pt	Ni	Fe	Cu	Ag
λ_0	191880	146000	127500	89440	89025	82060	71320
B. P. ..	6970°	5960°	4800°	3650°	3475°	3110°	2740°

The evaporation of metals heated in an atomic hydrogen flame was very rapid and gave results which confirmed the data on evaporation *in vacuo*. Jackson [6] extended his researches on secondary emission from molybdenum due to the bombardment of high speed positive ions of the alkali metals. Evidence was obtained that heat treatment of the molybdenum reduced the secondary emission.

Lenher and Fruehan [7] have investigated the crystal structure of seleno compounds of tungsten. They prepared crystals of ammonium selenotungstate, $(NH_4)_2WSe_4$, and of ammonium diselenotungstate, $(NH_4)_2WSe_2O_2$. The first were green and the second red. Both were readily soluble in water but insoluble in CS_2 and C_6H_6. The first are not isotropic and therefore not isometric. Optical study of the di-salt would lead to the conclusion that the crystals are triclinic and isomorphous with crystals of the corresponding sulfur salt, $(NH_4)_2WS_2O_2$.

[3] Davisson and Germer, *Phys. Rev.*, **30**: 634 (1927).
[4] Jones, Langmuir and Mackay, *Phys. Rev.*, **30**: 201 (1927).
[5] Forsythe and Worthing, *Astrophys. J.*, **61**: 146 (1925).
[6] Jackson, *Phys. Rev.*, **30**: 473 (1927).
[7] Lenher and Fruehan, *J. Am. Chem. Soc.*, **49**: 3076 (1927).

Alloys. Palmer [8] has published a very practical table on the various properties, applications, compositions, etc., of chrome and chrome-nickel steels. The exact properties of individual steels will vary considerably depending upon the percentage of C and Cr present and to a lesser extent upon special additions, such as Mn, Si, Cu, Al, W, and Mo. A few of the many properties recorded by Palmer are herewith tabulated:

	A	B	C
Analysis	Cr less than 14% C less than 0.4%	Cr more than 16% C less than 0.4%	Contain enough Cr and Ni to make steel austenitic.
Magnetic	Yes	Yes	No
Toughness	Structurally dependable	Low impact resistance	Varies with composition
Corrosion resistance	Resists water, weather and many organ. and inorgan. corroding agents.	Superior to A	Depends upon Cr % present; if over 16%, excellent.

Johnson [9] discusses at length the outstanding qualities of chrome-molybdenum steel which made up the framework of the famous Lindbergh plane and of other planes making record flights. The following analysis is called for in the U. S. army specifications and is used almost exclusively: C 0.25 to 0.35%; Mn 0.40 to 0.60%; Cr 0.80 to 1.10%; Mo 0.15 to 0.25%.

This material has excellent weldability and has air hardening properties in thin sections which are very desirable, since the tensile strength of a section close to the weld is not seriously affected. The tensile strength is nearly 100,000 lbs. per sq. in. The Cr-Mo steel gives excellent response to heat treatment.

Tests on a Cr-Ni steel at high temperatures were made by MacPherran.[10] The thermocouple was placed in the centre of the test specimen. The chemical composition and physical properties of the forged bars of Cr-Ni steel were as follows: C 0.46, Mn 0.58, Si 0.91, Cr 7.19, Ni 18.73%; tensile strength 105,550 lbs./sq. in.; elongation, 33% in 2 in.; reduction in area 53%. At over 760° C. this steel not only falls off in strength but becomes less ductile until a temperature of about 980° C. is reached. From

8 Palmer, *Chem. Met. Eng.*, **35**: 149 (1928).
9 Johnson, *Iron Age*, **131**: 1076 (1928).
10 MacPherran, *Proc. Am. Soc. Testing Materials*, **37**, pt. 2: 73 (1927).

this point on the strength continues to fall off but the ductility increases to a remarkable extent.

Of very special interest to chemists are the painstaking re-searches carried out at the Bureau of Chemistry and Soils, Wash-ington, on steels best suited for apparatus used in the fixation of atmospheric nitrogen. Thompson,[11] commenting upon the difficul-ties encountered, points out that the steel or other alloy must withstand pressures up to 1500 atmospheres and temperatures up to 500° C. From studies thus far it is evident that hydrogen, both molecular and atomic, is undoubtedly the principal agent in the destruction of the materials. The presence of nitrogen or nitrides in the higher chrome steels furnishes a clew as to the mechanism of attack and destruction of the metal walls during the synthesis of NH_3. The stable nitrides of chromium remaining in the steel structure—or the solid solution of nitrogen in the Cr-Fe matrix—apparently are impermeable to the gases and prevent or greatly retard further attack. Steels containing more than 2% Cr were the only ones to show this nitride formation. The steels which formed this nitride layer all exhibited satisfactory resistance to the action of the gases, N and H and NH_3. All evidence to date points to the desirability of a low carbon, chromium rich steel for the construction of NH_3 synthesis apparatus.[12]

[11] Thompson, *Iron Age*, **120**: 1518 (1927).
[12] For additional material see: Furness, U. S. Bur. Mines Infor. Circ. no. 6038 (1927); Hibben, *J. Am. Chem. Soc.*, **50**: 1118 (1928); Le Baron, *Chem. Met. Eng.*, **35**: 242 (1928); Mudge and Cooney, *Proc. Am. Soc. Steel Treating*, Sept., 1927; various articles on plating of chromium on steel, brass, etc., in *Trans. Am. Electrochem. Soc.*, **53**; *Brass World*, 1927 and 1928; *Metal Ind.* (New York), 1927 and 1928.

Chapter XIV.

Iron and Steel Metallurgy.

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Ferrous metallurgy may be fairly definitely divided into two classes: (1) physical metallurgy, or the study of the solid steel or iron and the effect of various elements and treatments on the properties of these materials; (2) process metallurgy, or the study of the conversion of the raw materials into the finished product.

In physical metallurgy, chemistry has played an important part, even though many physical metallurgists have not realized until the past few years that their "iron-carbon diagrams" are fundamentally physico-chemical. Progress in process metallurgy has always been, and still is, largely a matter of sound mechanical engineering combined with just enough chemistry to enable the steel producer to make the grade of steel required. In each class there is a wide field for the chemist. There is a splendid field for the physical chemist in physical metallurgy and a still greater field for him in process metallurgy, for steel-making is a chemical industry just as much as is the refining of oil, the burning of lime and the making of paper.

In this survey the attempt has been made to eliminate references wherein chemistry is not directly involved, and many excellent pieces of work which would be of some interest to the chemist have necessarily been omitted.

Direct Reduction of Iron Ore. A survey of methods for the gaseous reduction of iron ore is presented from the standpoint of equilibria involved, quality of steel produced and description of processes by Hodson, Emmett, Smalley, Stansfield, Wiberg and Kramers.[1] Important considerations are the amount of nitro-

[1] Hodson, *Trans. Am. Electrochem. Soc.*, **51**: 205 (1927); Emmett, *ibid.*, 207; Stansfield, *ibid.*, 217; Hodson and Smalley, *ibid.*, 225; Smalley and Hodson, *ibid.*, 247; Wiberg, *ibid.*, 279; Kamura, *ibid.*, 305.

gen in sponge iron compared to that in pig iron, the importance of diffusion on the rate of reduction in the various processes and the effect of surface exposed on the rate of reduction. Williams, Barrett and Larsen [2] have made a detailed study of the production of sponge iron and showed the feasibility of producing it at a price comparable with pig iron. If high sulfur fuel is used, high sulfur sponge iron will be obtained and all of the phosphorus in the ore will be left in the product. Furnas and Brown [3] have computed the equilibrium constants involved in the reduction of ferric oxide.

Blast Furnace. The most important developments are listed by Berg [4] as being the use of the larger furnace, the proper selection and sizing of raw materials and more complete gas cleaning. Dovel [5] describes construction changes in a blast furnace working with hard ores, which increased production 30% and cut down fuel consumption 16%. The production of high-alumina slags in an experimental blast furnace is reported by Joseph, Kinney and Wood.[6] These slags are suitable for the production of alumina cement, and with the slag is produced at times a pig iron extraordinarily low in sulfur. Herty and Gaines [7] have developed a theory of desulfurization in the blast furnace which is based on physicochemical relations between liquid slag and metal.

Cast Iron. An interesting development in the manufacture of cast iron pipe is described by McKenzie,[8] Capron [9] and Cammen.[10] The molten metal is poured into a mold which is either rotated while the metal is being poured or is rotated after pouring has ceased. It is claimed that the physical properties of the iron are improved over ordinary cast iron, the iron is denser and the use of cores is eliminated.

Open Hearth. The open hearth process is essentially a physico-chemical and chemical engineering operation. The reactions involved in refining steel are complex and the relations between slag and metal, both as regards rates of diffusion and equilibria, present a wide field for chemical research. The foremost mechanical achievement of the year was the erection and

[2] Williams, Barrett and Larsen, U. S. Bur. Mines, Bull. no. 270 (1927). 175 p.
[3] Furnas and Brown, *Ind. Eng. Chem.*, **20**: 507 (1928).
[4] Berg, *Blast Furnace Steel Plant*, **16** :15 (1928).
[5] Dovel, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 73 (1928).
[6] Joseph, Kinney and Wood. *Am. Inst. Mining Met Eng.*, Tech Pub. no. 112 (1928).
[7] Herty and Gaines, *Blast Furnace Steel Plant*, **16**: 233 (1928).
[8] McKenzie, *Iron Age*, **120**: 1302 (1927).
[9] Capron, *Blast Furnace Steel Plant*, **15**: 376 (1927).
[10] Cammen, *Trans. Am. Soc. Steel Treating*, **11**: 915 (1927).

operation of 250-ton stationary open hearth furnaces by the Weirton Steel Co., at Weirton, W. Va.[11] The advantages of the tilting furnace are described by Waterhouse,[12] who also remarks, in speaking of the reactions that take place in the open hearth: "It is now the custom to call this whole subject the physical chemistry of steel making——." Smith [13] describes in detail the manufacture of alloy steels and states that "in the present state of knowledge the skill of the maker is more important than the quantitative chemistry." Dornin [14] discusses deoxidation with special reference to the best methods of preventing oxidation of the steel bath. Slags low in iron oxide are particularly desirable. Herty and Gaines [15] determined the solubility of iron oxide in iron between 1,535 and 1,730° C. From 1,535 to 1,600° C., the normal steel-making range, the solubility increases from 0.94 to 1.36% FeO. Feild [16] calculated the amount of FeO which would be present in a bath of steel by combining equilibrium data and rates of diffusion between slag and metal. The oxidation of the steel depends, according to Feild, on the rate of carbon elimination and the temperature and on the iron oxide content of the slag.

Alloy Steels. Homerberg and Zavarine [17] have made a study of chromium-aluminum and chromium-nickel-aluminum steels. These steels compare favorably with structural alloy steels used in automotive construction and are not necessarily useful for nitrided articles only. Corson [18] reported at length on iron-silicon alloys, giving constitutional diagrams and physical properties in detail. Alloys containing 14.5 to 17% are most resistant to acid corrosion. Foley [19] described the difficulties in determining the elastic limit of steel at elevated temperatures and discussed methods by which the elastic limit at these temperatures may be calculated from tests at room temperature. French [20] has compared the alloying limits of chromium, nickel, molybdenum and vanadium in structural steels and has discussed many of the physical properties of these steels. French and Digges [21] also discussed the effect of antimony, arsenic, copper and tin in high-

[11] *Blast Furnace Steel Plant,* **15:** 55 (1927).
[12] Waterhouse, *Iron Age,* **121:** 1529 (1928).
[13] Smith, *Iron Age,* **121:** 1532 (1928).
[14] Dornin, *Trans. Am. Soc. Steel Treating*, **13:** 29 (1928).
[15] Herty and Gaines, *Am. Inst. Mining Met. Eng.* Tech. Pub. no. 88 (1928).
[16] Feild, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 111 (1928).
[17] Homerberg and Zavarine, *Trans. Am. Soc. Steel Treating*, **13:** 297 (1928).
[18] Corson, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 96 (1928).
[19] Foley, *Trans. Am. Soc. Steel Treating*, **13:** 813 (1928).
[20] French, *Trans. Am. Soc. Steel Treating*, **11:** 845 (1927).
[21] French and Digges, *Trans. Am. Soc. Steel Treating*, **13:** 919 (1928).

speed steel and showed that these elements adversely affected the hot-working properties and reduced tool life in the finish-turning tests. He concluded that the permissible limits for each of the elements depend upon the character of service for which the steel is intended. (Prevention of the introduction of such elements into steel is an important question today and until means are found for their elimination from steel they will gradually build up in concentration in all steels.)

Corrosion. Mitchell [22] has discussed new alloys for the control of corrosion. The important points in the use of an alloy steel are that only alloys which are true solid solutions should be used as base metals and that any salts formed by corrosion should be as insoluble as possible, thereby utilizing the protective coating to the best advantage. Fraser, Acreman and Sands [23] pointed out methods for controlling variables in the quantitative study of submerged corrosion of metals; the most important variables are: concentration of dissolved oxygen, velocity of relative motion between test pieces and solutions and temperature.

Dorsey [24] described the effect of degasification of metals and protective coatings to reduce corrosion. Russell, Chappell and White [25] determined the effect of velocity on the corrosion of steel under water. The presence of a rust film greatly alters the corrosion rate and under this condition increase in velocity increases the rate of corrosion. This action may be reversed if the steel is cleaned and polished.

Chappell [26] showed that the thicker the rust film the slower the corrosion rate. In the absence of rust films, rates are determined by the chemical properties of the steel surface. Copper-bearing steels are discussed. Intercrystalline corrosion of metals was discussed by Rawdon.[27]

Fluxes and Refractories. Bowles [28] described the factors affecting the economical use of metallurgical limestone and dolomite and pointed out many of the qualities desired in both blast furnace and open hearth limestone. Herty [29] compared burned lime and raw limestone in the basic open hearth process, with par-

[22] Mitchell, *Ind. Eng. Chem.*, **19**: 1253 (1927).
[23] Frazer, Acreman and Sands, *Ind. Eng. Chem.*, **19**: 332 (1927).
[24] Dorsey, *Ind. Eng. Chem.*, **19**: 1219 (1927).
[25] Russell, Chappell and White, *Ind. Eng. Chem.*, **19**: 65 (1927).
[26] Chappell, *Ind. Eng. Chem.*, **19**: 464 (1927).
[27] Rawdon, *Ind. Eng., Chem.*, **19**: 613 (1927).
[28] Bowles, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 62 (1928).
[29] Herty, *Ind. Eng. Chem.*, **19**: 592 (1927).

ticular reference to the type of open hearth charge. Beecher [30] called attention to the important properties of special refractories such as mullite, aloxite and carborundum. The four principal causes of failure in refractories are classified as plastic distortion, permanent volume change, spalling and chemical attack. Each of these causes is discussed in some detail. The factors affecting open hearth refractories are discussed at length by Larsen and Grodner, [31] with especial reference to the effect of temperature changes in the furnace.

Miscellaneous Research. The deterioration of steel in ammonia has been investigated by Vanick, [32] who found that a suitable steel for the prevention of fissuring and decarburization should contain at least 2.25% chromium and not more than 0.30% carbon. He discussed other alloy steels.

A complete treatise on ingot iron by Kenyon [33] described many physical properties of this material. Parr and Straub [34] discussed the embrittlement of boiler plate, with reference to caustic concentration in the boiler water and stress in the steel.

General Chemical Problems of the Industry. Mathews [35] discussed the application of metallurgy to motors and described improved methods in the manufacture of electric furnace steel. Forbes [36] gave a complete account of the technologic problems of the steel industry; the rôle which chemistry can play in the solution of these problems will be very evident to the careful reader of that paper. A comprehensive survey of the advance in physical chemistry in steel-making was given by Larsen [37] and Herty [38] described the fundamental factors involved in the elimination of nonmetallic inclusions from steel. These four articles describe the field for the chemist, and particularly the physical chemist, in the steel industry.

In conclusion, it may be said that the steel maker is becoming more and more interested in chemistry and is beginning to realize the advantages to be gained from fundamental research in his field. During the past year the United States Steel Corporation created a Department of Research and Technology with Dr. John

[30] Beecher, *Trans. Am. Soc. Steel Treating*, **13**: 473 (1928).
[31] Larsen and Grodner, *Blast Furnace Steel Plant*, **15**: 217 (1927).
[32] Vanick, *Trans. Am. Soc. Steel Treating*, **12**: 169 (1927).
[33] Kenyon, *Trans. Am. Soc. Steel Treating*, **13**: 240, 435 (1928).
[34] Parr and Straub, *Ind. Eng. Chem.*, **19**: 621 (1927).
[35] Mathews, *Ind. Eng. Chem.*, **19**: 1089 (1927).
[36] Forbes, Yearbook Am. Iron Steel Inst., **1927**: 237
[37] Larsen, *Blast Furnace Steel Plant*, **15**: 10 (1927).
[38] Herty, *Trans. Am. Soc. Steel Treating*, **11**: 264 (1927).

Johnston as director.[39] Thirty steel companies are coöperating with the U. S. Bureau of Mines and the Carnegie Institute of Technology in a study entitled "The Physical Chemistry of Steel-Making." A number of companies are expanding their laboratories and beginning research in the true sense of the work.

Suggested Research Problems

The following are suggested as research problems:

1. Determination of the effect of temperature on the solubility of carbon in liquid iron in the presence of silicon and manganese.

2. The equilibrium between carbon, iron and oxygen above the melting point of iron.

3. Methods for determining iron sulfide and manganese sulfide in steel.

4. Methods for determining manganese oxide in steel.

5. Physical properties of steels at elevated temperatures.

6. Equilibrium diagram of the system $FeO-MnO-SiO_2$.

[39] *Ind. Eng. Chem.*, **19:** 766 (1927).

Chapter XV.

Lead.

Gustave W. Thompson,*

Chief Chemist, National Lead Company

The important features of the lead industry during the past year were principally those affecting the supply, from both primary and secondary sources. There have been no revolutionary discoveries but rather a continued development toward better methods in which chemistry has played the major rôle.

Production. While the world figures show a small increase over the previous year's, production in the United States declined, following the sustained drop in the price of the metal. Consumption figures, more difficult to determine with accuracy, will probably show a slight increase on a world basis, although here again, the figures for the United States declined. The increase in world production was due to the larger output in Mexico, while the increased demand, in spite of a domestic drop, must be laid to the improved industrial conditions in Europe, especially England and Germany.

It is worth while to mention in passing the only new ore deposit of commercial proportions. This potential producer is the Buchans Mine in Newfoundland, the ore bodies in which were found by electrical prospecting methods.

Ore Treatment. *Hydrometallurgy.* By far the outstanding feature of the entire lead industry has been the development of selective flotation. Clinton H. Crane, President of the St. Joseph Lead Company, estimates [1] roughly the following increase in production due to selective flotation: Canada, 110,000 tons or 73% of its total; United States, 110,000 tons or 15%; Mexico, 70,000 tons or 26%; North America, 290,000 tons or 26%; the entire world, 440,000 tons or 24% of the total production.

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* Assisted by L. H. Schroeder and G. O. Hiers.
[1] Crane, *Eng. Mining J.,* **125**: 85 (19282).

The enormous existing tonnage of low grade lead-zinc sulfide ores is beginning to be tapped just as the richer deposits of galena are showing some signs of depletion. In order to utilize these low grade ores economically, it was necessary to secure a better separation of lead and zinc minerals than had heretofore been possible. Results have now been obtained which establish good separation into marketable concentrates. It is true that there has been some further improvement in equipment represented by the new type of pneumatic flotation machines, using from 2 to 3 pounds air pressure, but the salient factor in flotation progress has been the development of chemical "addition agents," the reagents which cause a selective wetting of sulfide particles in the froth. The oils formerly used as frothing agents are still used but in greatly reduced quantities.

A number of special selective agents have come into use during the last few years, such as potassium xanthate. Xanthate was considered the best reagent a year ago and is still widely used in conjunction with the older reagents, especially since the litigation which formerly tied up its use has now been favorably settled. More recently, however, several newly discovered agents, which show signs of great promise in the lead-zinc field, have been coming to the fore.

Thiocarbanilide is said to have a greater selective action and less tendency to promote bulk flotations of all sulfides. Phosphocresylic acid, originally devised for the selective flotation of copper minerals from pyrite, is finding use in separating lead and zinc minerals. Still others, which it is unnecessary to name, show signs of promise in selective work.

There is one factor in connection with selective flotation which it seems worth while to mention here, that is, its influence on lead smelting practice. The lowering of the zinc content of lead concentrates has lessened slag troubles and made for a reduction in fuel. On the other hand, the fine condition of the charge has increased the problem of its preparation for the blast furnace and double roasting is largely being resorted to for overcoming this difficulty.

With the basic patents expiring and litigation gradually reaching settlement, we may expect further developments in flotation in the near future.

In the hydrometallurgical field there is little further to be said.

The acid-brine leaching processes are still being developed and may become important in the future.

The Bunker-Hill & Sullivan Company has brought to a more successful operation its electrolytic lead plant at Kellogg, where tailings are treated in a Tainton cell and the deposited metal recovered on a moving cathode.

Pyrometallurgy. There have been no great changes in the field of pyrometallurgy. The further installation of the Newnam mechanical scotch hearth furnaces in the great Federal lead smelter at Alton, Illinois, the new smelter of the Phelps-Dodge Corporation at Douglas, Arizona and the additions to the new smelter of the National Lead Company, at Buenos Aires, South America may be mentioned.

Secondary Lead. The secondary lead recovered in the United States has been estimated to be over 250,000 tons during the past year. This tonnage will no doubt be increased since a great deal of attention has been directed to the problem of recovering lead from scrap.

In the caustic soda processes, as exemplified by the Harris and the Thompson processes, a considerable improvement in knowledge and efficiency of the processes has been gained by plant scale operation and experimental work. The production of soft lead (which needs only desilverization), antimonial lead and tin in place of the usual junk white metal produced in ordinary secondary smelting operations, is a problem which the above processes are solving.

Reclamation [2] of storage battery lead scrap by the Ford Motor Company at Highland Park was another development of interest during the year. The scrap was reduced with charcoal in suitable shaft furnaces and the antimonial lead obtained used for new battery grids.

No startling developments have taken place in the manufacture of white lead or lead oxides, nor was such a thing to be expected.

Physical and Chemical Studies. Lead isotopes have come in for further study during the past year. Aston,[3] using lead tetramethyl procured from the Geophysical Laboratory at Washington, obtained the mass spectrum of ordinary lead. To quote the author, "The principal lines are 206(4), 207(3), 208(7). The figures in brackets indicate roughly the relative intensities and

[2] Huntley, *Metal Ind.*, **25**: 447 (1927).
[3] Aston, *Nature,* **120**: 224 (1927).

are in good agreement with the atomic weight 207.2. There are indications that many other isotopes may be present in small proportions. An exceedingly faint line at 209 occurs in the atomic group and on one plate, is visible on the $PbCH_3$ group. This is almost certainly an isotope." The evidence suggests the possibility of the existence of isotopes of 203, 204, and 205 atomic weights. Since ordinary lead is not radioactive it may be deduced from the above data that the isotopes of lead heretofore isolated owe what radioactivity they have had to residual traces of radioactive elements present as impurities.

A special committee of the American Society for Testing Materials has undertaken the problem of the determination of particle size and shape of sub-sieve sizes, *i.e.*, sizes under seventy-five microns in diameter. One of the samples used was red lead and studies of this nature will undoubtedly prove of value in the manufacture and use of storage batteries and pigments.

The use of red lead and litharge as catalysts [4] in the hydrogenation of nitrobenzene to aniline was studied by several co-workers. Litharge proved to be the best and was selected for further experimentation.

A symposium on lead held at St. Louis, Missouri, December, 1927, under the auspices of the American Institute of Chemical Engineers brought forth many interesting papers. Among those presented was one on the use of lead compounds in rubber manufacture. Other papers pertaining to the mechanical properties of lead and its alloys, and also to corrosion resistance were presented. Considerable attention is being given to the study of fatigue failures of lead. Such failures occur where lead is subjected to excessive mechanical vibration. Alloying with antimony, tin or cadmium strengthens the lead and tends to prevent failure. Corrosion sometimes accompanies and accelerates such failures.

Hull and Steele [5] have made ingenious use of a quartz spectrograph in the analysis of lead and its alloys. The standard used as a practical "spectrographically pure lead" was described on page 32 of Vol. I of the Annual Survey. Other standards of pig lead and alloys containing maximum permissible impurities were also made up so that, by comparison, it could be ascertained whether or not newly purchased supplies of metal were sufficiently pure.

[4] Madenwald, Henke and Brown, *J. Phys. Chem.*, 31: 862 (1927).
[5] Hull and Steele, *Am. Soc. Testing Materials*, 81 (preprint) (1927). 14 p.

During the annual convention week of the American Institute of Mining and Metallurgical Engineers in February, 1928, many interesting discussions came up, both at the symposium on secondary metals and at the session on lead. Particularly worth mentioning were the pertinent suggestions for overcoming the difficulties in evaluating secondary metals by proper sampling for chemical analysis. Several papers were also presented on the constitutional equilibrium diagrams of lead alloys.

Papers on lead storage batteries and the corrosion of lead were presented at the American Electrochemical Society meeting during April, 1928. The Bureau of Standards is continuing the study of lead storage batteries. At the Fall meeting of the American Chemical Society at Detroit, Michigan, several papers on the surface tension of lead-tin solders and fluxes were presented.

Other studies which deserve mention are the working out of phase diagrams of the systems lead-sulfur-oxygen [6] and iron-lead-sulfur.[7] The system lead-sulfur-oxygen is particularly important in connection with the roasting of galena and a solid model for the pressure, temperature, composition relations was well worked out by a German worker.

[6] Schenck, *Metall. u. Erz*, **23**: 407 (1926).
[7] Leitgebel, *Metall. u. Erz*, **23**: 439 (1926).

Chapter XVI.

Magnesium and Beryllium.

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Magnesium. The continued growth of the magnesium industry is shown by the following figures taken from the annual reports of the Bureau of Mines, Department of Commerce.

Year	Sales		Average Ingot Price
	Pounds	Value	Per Pound
1921	48,000	$ 86,000	$1.30
1922	60,000	89,000	1.60
1923	125,000	155,000	1.25
1924	128,000	150,000	1.07
1925	245,000	274,400	0.86
1926	322,650	390,400	0.80
1927	366,400	441,700	0.68

Sales of castings and wire were slightly less than in 1926, but this was offset by an increase of 94% and 159% in tubing and sheet metal respectively.

Present demands for metal are considerably greater than production, which it is estimated will increase 50% during 1928. It is expected, however, that the current metal shortage will be met by plant extension programs now in progress.

Cook and Jones [1] have continued their investigations on the magnesium-copper series. A thorough study was made of the forged and forged heat-treated alloys containing 0 to 11% copper. The strength increases with increasing copper content up to 2%, after which it remains constant throughout the range investigated, while the ductility shows a continuous decrease. Heat treatment produced no beneficial results.

[1] Cook and Jones, *J. Inst. Metals*, **38**: 103 (1927).

Hume-Rothery and Rowell [2] investigated the magnesium-cadmium alloys. Based on thermal analyses and microscopic examinations, a new constitutional diagram was constructed. No confirmation was obtained for the presence of the compound $MgCd$, but their data show the existence of the compound $MgCd_2$.

Meissner [3] studied the age-hardening of six commercial magnesium alloys of the Electron type; namely, magnesium-aluminum, magnesium-zinc and magnesium-aluminum-zinc alloys. In no case was room temperature hardening observed, but artificial hardening at somewhat higher temperatures was obtained on all compositions containing more than 6% aluminum or 2% zinc.

The constitution of the magnesium-zinc alloys has been redetermined by Chadwick. [4] No great change was found in the liquidus, but the solidus was greatly modified. A new compound $MgZn_5$ was found. The solid solubility of zinc in magnesium is considerably higher than that reported by Meissner.

A metallographic study of magnesium has been reported by Pulsifer. [5] It consists of a series of photomicrographs of cast and worked magnesium as developed by deep etching of roughly polished specimens.

Mathewson and Phillips [6] have measured the twinning angles in magnesium crystals.

Keyes [7] gives a review of laboratory research work on different methods of manufacturing magnesium. Best results were claimed for the electrolysis of a bath of MgF_2 containing small amounts of other fluorides.

Gann and Winston [8] have given a general résumé of the magnesium situation. An exceptionally pure commercial metal is now available, analyzing $99.9 + \%$ magnesium. The more important binary alloys are reviewed from the standpoint of properties and structure. The development of polynary alloys is then discussed. A complete disclosure is made of the melting, alloying and casting practice involving the use of a flux. Many magnesium alloys may be heat treated and fabricated. One of the best protective coatings thus far developed consists of a primer coat formed by a hot acid phosphate dip followed by aluminum bronze in a rubber

[2] Hume-Rothery and Powell, *J. Inst. Metals,* **38**: 137 (1927).
[3] Meissner, *J. Inst. Metals,* **38**: 195 (1927).
[4] Chadwick, *J. Inst. Metals,* Advance copy no. 449 (Mar., 1928).
[5] Pulsifer, *Am. Inst. Mining Met. Eng.,* Tech. Pub. no. 42 (1928).
[6] Mathewson and Phillips, *Am. Inst. Mining Met. Eng.,* Tech. Pub. no. 53 (1928).
[7] Keyes, *Trans. Am. Electrochem. Soc.,* **51**: 197 (1927).
[8] Gann and Winston, Ind. Eng. Chem., **19**: 1193 (1927).

paint vehicle. Press-forged magnesium alloy pistons of high strength and improved thermal conductivity are a recent successful development.

An excellent compilation of much of the existing literature on magnesium and its alloys appears in the book "Light Metals and Alloys." [9] The value of this publication has been enhanced by a bibliography containing approximately 200 citations.

Beryllium. The literature dealing with the metallurgical applications of beryllium contains many contradictory statements, largely due to the newness of the subject. Many claims have been made relative to the improved properties obtained by additions of small percentages of beryllium to various metals, while others question whether such compositions will have properties not possessed by other alloys.

Reviews of the different methods of producing beryllium are given by Illig [10] and Kroll.[11] Recent quotations were approximately \$200 per pound but lower prices can be expected with increased production.

Beryllium has been considered as an alloying ingredient chiefly in aluminum and copper alloys. Kroll [12] showed that beryllium can successfully replace silicon in aluminum-magnesium alloys insofar as it forms compounds with magnesium that are soluble in aluminum. The optimum advantage occurs at 6% beryllium, but the effect per unit weight is less than in the case of silicon.

Archer and Fink [13] have made the most complete study of the aluminum-beryllium alloys. Their investigations include the constitutional diagram, microstructure, heat treatment and properties of alloys containing up to about 2% beryllium. Less than 0.1% beryllium is soluble in aluminum at the eutectic melting point $631°$ C. and this decreases to approximately 0.01% at room temperature. An increase of $50\text{-}60\%$ in both strength and hardness was observed on some of these alloys after subjection to age-hardening.

Corson [14] studied the copper-beryllium and copper-nickel-beryllium alloys. Age-hardening occurs in both series, although in the latter case the precipitated compound remains ultramicroscopic.

[9] U. S. Bur. Standards, Cir. no. 346 (1927).
[10] Illig, *Z. Metallkunde,* **18**: 159 (1926).
[11] Kroll, *Metal Ind.* (*London*), **30**: 357 (1927).
[12] Kroll, *Metall Erz.,* **23**: 613 (1926).
[13] Archer and Fink, *Am. Inst. Mining Met. Eng.,* Tech. Pub. no. 91 (1928).
[14] Corson, *Brass World,* **22**: 314 (1926).

Photomicrographs and mechanical properties of copper-beryllium alloys are given.

Bassett [15] likewise investigated the copper-beryllium alloys. Hard drawn wires possessed high tensile strength coupled with good conductivity. The corrosion of these alloys approximates that of pure copper. The additions of small amounts of cadmium, tin or aluminum to copper-beryllium alloys resulted in but small additional property improvements. Possible applications for these alloys are for springs, strong wire, and high strength conductors.

Masing [16] and Dahl [17] have investigated the alloys of beryllium with copper, nickel, cobalt, and iron. They conclude that beryllium produces much more beneficial effects when added to these heavy metals than when added to aluminum. An age-hardened copper alloy containing 3% beryllium had a tensile strength of 215,000 pounds per square inch, while the addition of 3 to 4% beryllium to copper, nickel, cobalt or iron gave Brinell hardness of 525-660.

Becker [18] states that beryllium can be made into very light thin membranes that are seventeen times more permeable to X-rays than aluminum.

An excellent metallurgical résumé of beryllium is given in the book "Light Metals and Alloys." [9]

[15] Bassett, *Proc. Inst. Metals*, **1927**: 218.
[16] Masing, *Z. Metallkunde*, **20**: 19 (1928).
[17] Dahl, *Z. Metallkunde*, **20**: 22 (1928).
[18] Becker, *Z. Elektrochem.*, **33**: 181 (1927).

Chapter XVII.

Zinc.

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Slab Zinc Manufacture. *Continuous Retorts.* The most in-
teresting news in the field of zinc and zinc compounds in the past
two years is the report that the New Jersey Zinc Company has
successfully developed a large continuous retort and has begun
the construction of a commercial plant. The literature, both patent
and otherwise, describes many attempts to produce metallic zinc
in continuous retorts of relatively large size, both with a briquetted
and a loose charge, but either through an incomplete understand-
ing of the difficulties involved or a lack of sufficient financial
backing to carry the ideas through the expensive development
steps that such a radical change from present practice requires,
none of these previous attempts has been successful enough to
lead to a large commercial installation.

There is no publication or public disclosure of the new process
other than that revealed in British Patent Specification 269,324,
which was filed on April 10, 1926, and accepted as complete on
April 21, 1927. The specification and claims in this patent
call for the treatment of mixed ore and reducing agent (coal)
briquettes large enough so that the mass within the retort is porous
to the rising currents of gases which may channel back and forth
from the side walls to the center, and thereby heat up and reduce
the charge in the center of the retort as well as the charge at the
side walls. The disclosure further states that the zinc may be
worked off of such a descending column of briquettes without
fusing or sintering the charge, and that the briquettes may even
be drawn off at the bottom of the retort as a pulverent residue.

The advantages claimed for the new process are higher re-
coveries, lower fuel and labor costs and a more uniform and
higher grade product.

The retort process for the production of metallic zinc with its multiplicity of small expensive distilling vessels, its hand labor and low output per unit has been the butt of metallurgical jest for many years. The electrolytic process, which has come so much to the fore in the last decade, was a great step in advance. Its greatest success, however, has been on mixed ores where the removal of the zinc is essential to the economical treatment of the ore for the balance of the values contained therein. It has not yet succeeded in displacing the retort process on ores of zinc alone. Judging from what is heard of this new development of the New Jersey Zinc Company, the pyro-metallurgists have at last started a counter attack and the electro-metallurgists will need to move fast to keep their present lead.

Sintering. More Dwight Lloyd sintering machines for removing the last 2 or 3% of sulfur from roasted ore have been installed and their success has been amply demonstrated. The sulfur is removed to such a low point and the ore densified so thoroughly by this treatment that the capacities of retorts have been materially increased, while the recoveries have gone up at the same time. Also by leaving from 2 to 3% of sulfur in the roast the capacity of the roasters is increased and the costs of roasting decreased.

Best results in sintering seem to be obtained where about 5% of fine coal is mixed with the ore. This practice gives a better product and is much more fool-proof than the earlier scheme of leaving 6 or 8% of sulfur in the preroast and depending on this to supply all the heat needed on the sintering machine.

Waelz Process. The Waelz process, which involves furnacing mixtures of low grade zinc ores and coal in a rotary kiln, internally fired with fuel oil or pulverized coal, for the volatilization of the zinc and production of a low grade by-product zinc oxide, is to receive a large scale commercial trial in this country by the Steel Corporation at its Donora plant where the retort residues are to be treated by this process. Other trials of the Waelz process in this country are under consideration, the most promising of which contemplate the production of by-product zinc oxide for electrolytic zinc or lithopone production from mine or mill tailings too low to treat in the ordinary fashion for metal or oxide.

Improved recoveries due to using sintered ore have reduced the zinc in ordinary spelter residues so that it hardly pays to treat them in the Waelz kiln unless the furnaces are intentionally operated to give high zinc residues. Owing to the fact that the

production of zinc is very much more rapid during the first three-quarters of the present standard 24-hour cycle than in the last quarter and that higher temperatures are needed to remove the zinc that is obtained at the end with consequent severe conditions for the retorts to withstand, it is possible that real economies can be obtained by reducing the retort cycle to 18 hours or less, doing away with the high finishing temperatures now used and depending on the Waelz process to recover the zinc left in the residues and return it to the process. It is understood that some such plan as this is contemplated at the United States Steel Corporation's plant at Donora.

The product of the Waelz process is an impure zinc oxide which can only be sold as a zinc concentrate. Due to its fine powdery condition it is not desired in large amounts by ordinary zinc smelters but will find an outlet in electrolytic zinc and in lithopone manufacture. Even in the electrolytic process the absence of other values makes it an expensive source of zinc, while litho-pone manufacturers are so particular about the chemical composition of their zinc material as to make them difficult customers to please. It is probable therefore that Waelz kiln installations will be limited to large companies who will plan to absorb the whole product in their own operations.

Electrolytic Zinc. The production of electrolytic zinc continues to expand. The Anaconda Copper & Mining Company and the Consolidated Mining & Smelting Company have completed large additions to their plants, and the new plant of the Bunker Hill & Sullivan Co. at Kellogg, Idaho, has just started up. The essential difference between this plant and that of the other existing electrolytic plants is in the higher current densities employed at Kellogg whereby economies in initial plant outlay are claimed to be realized. Higher acid concentrations of the electrolyzing solution are also to be used here, which should result in a higher degree of purity of the metal. It is too early yet to determine whether these experimentally demonstrated advantages will be realized economically.

Slab Zinc Consumption. *General.* The ever increasing production of electrolytic high grade metal is paralleled by a steadily growing demand which, to a considerable extent, is the direct result of technical investigations which have demonstrated that its high purity is of the greatest advantage for certain uses.

Rolled Zinc. The use of high grade zinc by zinc rollers is

steadily increasing. Strip made from this grade of metal has unusual ductility and its adaptability to difficult drawing and forming operations has made it a popular substitute for the more expensive copper, brass and aluminum in many cases. High grade metal is being added to rolling mill mixes of selected grades of Prime Western Spelter to uniform the composition and control such important impurities as cadmium, lead and iron which have a marked influence on the physical properties of the rolled metal.

Zinc Base Alloys. In the field of die casting, zinc base alloys are growing in popularity. New patented alloys,[1] similar to the old 4% aluminum, 3% copper, 93% zinc, but containing additions of 0.1% magnesium or magnesium with small amounts (0.5%) of nickel, represent the latest development in this type of alloys. Greater tensile and impact strength and greater resistance to intercrystalline oxidation which causes warping and swelling, are claimed for these alloys. As in the case of the old 4% Al, 3% Cu alloy, the zinc used must be the high grade metal as low in the impurities lead, cadmium and tin as possible, in order to secure the above improvement in properties.

Galvanizing. Galvanizing continues to be the major outlet for slab zinc, consuming between 45 and 50%. High grade metal is being used to a greater extent for the production of heavily coated wire and sheets, where the good bending properties of the coating is essential. The malleability of the zinc coating is still commanding the attention of the more progressive producers. Several new patented processes have made their appearance during the past year, which secure the desired coating malleability through heat treatment of the galvanizing wire, or special pretreatment of the bare steel surface before galvanizing.

The American Society for Testing Materials has issued a number of tentative specifications for galvanized iron and steel products. The atmospheric exposure tests of galvanized sheets by Committee A-5 have begun to show failure of the light coated sheets after approximately three years' exposure in industrial atmospheres.

Theoretical Metallurgy. The contributions of Hoyt,[2] Mathewson and Phillips,[3] and Mathewson [4] to the technical literature have given us much useful information on the behavior

[1] Peirce and Anderson, U.S.P. 1596761 (Aug. 17, 1926).
[2] Wilson and Hoyt, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 25 (1927), 29. p.
[3] Mathewson and Phillips, *Am. Inst. Mining Met. Eng.*, Tech. Pub. no. 5 (1928). 8 p.
[4] Mathewson, *Proc. Am. Inst. Mining Met. Eng.*, Preprint, 1928, 7 p.

of zinc crystals under stress. Mathewson's studies of the process of twinning in zinc crystals and his conclusions regarding the functions of such twinned crystals in increasing the ductility of the metal when stressed, by presenting additional planes of slip favorably inclined to the application of the forces, are not only important additions to the metallography of zinc but are significant in their possible application to the study of other metals in which twinning is a common phenomenon.

Of general scientific interest is the development of spectroscopically pure zinc by Howard Cyr [5] of the Research Laboratories of the New Jersey Zinc Company. An arc struck between two crystals of this pure metal when examined with a large spectroscope shows only the lines of zinc.

Van Dycke, Peirce and Anderson [6] have completed an investigation of the alleged allotropic forms of zinc and found no such allotropic change in zinc over a wide range of temperature. They concluded that previous investigators, claiming to have found allotropic modification, were probably misled through the use of impure zinc.

Lithopone. Of the zinc compounds other than metallic zinc, lithopone continues to occupy the most promising position. The growth of this pigment has been phenomenal in the last fifteen years and the curve of increasing consumption has not as yet given any indication of flattening out. In 1927 the consumption of lithopone in the United States was 176,994 tons, an increase of 17,000 tons over 1926. In 1926 more lithopone was used than any other white pigment. Its increased consumption in 1927 still further increases this lead.

Normal lithopone contains approximately 28% of zinc sulfide and the valuable properties of the lithopone (color and hiding power) are attributed largely to this compound. It is not strange, therefore, that with the demand for less coats of paint on a given job, the zinc sulfide content of lithopone should be increased above that obtained in the normal precipitation of zinc sulfate by barium sulfide. These high strength products are obtained by adding zinc sulfide, as such, to normal lithopone, or by adding zinc chloride to the zinc sulfate solution before precipitating with barium sulfide. The usual concentration of the so-called high strength lithopone is 50% zinc sulfide. Such products are being made and sold in

[5] Cyr, *Trans. Am. Electrochem. Soc.*, **52**, preprint, 1927.
[6] Peirce, Anderson and Van Dycke, *J. Franklin Inst.*, **200**: 349 (1925).

increasing tonnages both here and abroad, their consumption being stimulated further by competition with the titanium pigments which have very high hiding power and have found a growing use in the paint, rubber and plastic fields. Lithopone titanium mixtures containing 15% of TiO_2, either admixed with the lithopone or muffled with the lithopone in the process of manufacture, are appearing on the market and have properties which make them very desirable pigments, the titanium oxide imparting a certain amount of anti-yellowing characteristic to the lithopone and a degree of weathering resistance in exterior exposures, in both of which properties lithopone benefits by reinforcement with other pigments.

Zinc Oxide. Nothing unusual has developed during the year in the manufacture of zinc oxide. There is a definite trend towards a more careful control of the furnaces so as to produce oxide which is better suited physically for specific uses, particularly rubber, while there has been a noticeable improvement in the color and smoothness of the paint grades.

Rubber manufacturers continue to be the largest consumers of zinc oxide. A better understanding of the chemical action of zinc oxide in compounded rubber, together with its well-known ability to produce a rubber which will stand heavy and rapidly repeated shocks without dangerous heating, has somewhat stabilized its position as a rubber reinforcing agent. However, its high volume cost as compared with other reinforcing pigments and with rubber itself still makes it the target for all cost cutting campaigns.

Zinc oxide holds a unique position in outside paints which is being more clearly recognized all the time. Due to its opacity to ultraviolet light and its ability to chemically stabilize the film, it is coming to be regarded as an essential ingredient in all high grade paints which must stand exposure to the weather no matter what other pigments are used.

On the other hand, it is meeting increasingly severe competition from lithopone in interior enamels and from the high hiding power pigments like zinc sulfide, high strength lithopone and the titanium pigments in lacquers.

The Future. Although in these days of intensive research and development it is dangerous to make specific predictions as to what will or will not be done in the next year or two, no one at all familiar with the trends in the zinc industry can be blind to the

fact that the days of rule of thumb production methods and stand-pat improvement policies are rapidly drawing to a close.

Large continuous retorts are bound to come sooner or later. They will require large original investments, but once built, operating economies, together with a more uniform and perhaps higher grade product, will give them command of the common metal market. By using selected ores they are likely to compete strongly with the electrolytic plants in the high grade market.

On the consumer's part a better knowledge of the exact composition of metal required for his special purpose with resulting more rigid specifications and a willingness to pay slight premiums if he has to, makes more careful control in the smelter profitable as well as necessary.

In the pigment field this trend toward process improvement and better plant control is even more noticeable. Modern lithopone is a quite different product from that of even two or three years ago, and the end is not yet in sight. Much of this development has been in the direction of designing the pigment for specific purposes and is the result of careful laboratory study of each step followed by strict plant control. In zinc oxide manufacture the practice of producing both paint and rubber oxide on the same furnace at the same time is waning. The modern practice is rather to so control the charge and the furnace that the product will be specially suited to either paint or rubber manufacture as the case may be. Even further specialization is probable in the future.

The zinc industry, of course, is not unique in its tendency towards more efficient production and improved product. It is merely keeping up with the general trend in all industry. Its progress in the last few years has been so much accelerated, however, that it is now entitled to be considered as one of the most progressive of the metallurgical industries.

Chapter XVIII.

The Rare Earths.

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The group of elements long designated as the "Rare Earths," has for many years possessed a great attraction to the original investigator until one by one the missing elements in this interesting group have been identified and their characteristics described. Spencer,[1] an international authority and writer concerning these particular elements, has made a valuable contribution upon "The position of the elements of the rare earths in the periodic system."

Illinium. The announcement in March, 1926,[2] that the last gap had been filled by the discovery by Hopkins, of element No. 61, or "Illinium," brought out the extremely interesting information that other investigators had been engaged in a similar search. This was covered in some detail in Vols. I and II, but during the last year still further contributions to the literature have been noted. Rolla and Fernandes[3] still claim priority in this discovery and, replying to Noyes,[4] contend that the experiments of Kiess[5] and of Yntema[6] offered only circumstantial evidence of the existence of element No. 61 and that the X-ray results reported by them constituted the first and only direct evidence of its existence.

They, therefore, claim the discoverer's right to name the element "Florentium." Noyes[7] takes exception to the contention of the two Italian chemists and maintains the priority of the work of Hopkins. In a paper presented before the Franklin Institute

[1] Spencer, *J. Am. Chem. Soc.,* **50:** 264 (1928).
[2] Harris and Hopkins, *J. Am. Chem. Soc.,* **48:** 1585 (1926).
[3] Rolla and Fernandes, *Nature,* **119:** 637 (1927); *Gazz. chim. ital.,* **57:** 290 (1927); *Chim. and ind.,* **18:** 394 (1927).
[4] Noyes, *Science,* **65:** 160 (1927).
[5] Kiess, Bur. Standards Sci. Paper no. **442:** 201 (1922).
[6] Yntema, *J. Am. Chem. Soc.,* **48:** 1598 (1926).
[7] Noyes, *Science,* **65:** 615 (1927).

in Feb., 1927, Hopkins [8] refers to the claim of Rolla and to the published account [9] of the latter's work that had been deposited with the Italian Academy in 1924. In this connection Hopkins calls attention to the publication by the U. S. Bureau of Standards, Jan. 6, 1922, of the wave-length of 130 arc-spectrum lines while 5 additional lines were published Sept. 29, 1923.[10] Prof. Rolla began his work early in 1922, deposited his sealed statement in June, 1924, and published it in Nov., 1926. Rolla and Fernandes [11] have described in considerable detail the method of separation employed by them using $TiNO_3$ and NH_4NO_3 and have applied it to the isolation of element No. 61 from one ton of didymium nitrate. Other researches on this new element are being vigorously prosecuted and further contributions concerning it may be anticipated.

Hafnium. von Hevesy, one of the discoverers of hafnium, has published in book form a history of this element in the German language. Brophy and Davey [12] give a method of separating zirconium and hafnium by the citrate method. Zirconium citrate, which is soluble in NH_4OH or citric acid solution, is sparingly soluble in water, while hafnium citrate is readily soluble.

There have been a number of general articles on the separation of zirconium and hafnium in the American chemical literature but no results of research investigations have been published. The existence of hafnium is well established, however, and its properties have been previously described. In view of the assertions by Urbain that element No. 72 (hafnium) was found by him in the more soluble fractions of the yttria group, Holton and Hopkins [13] applied the method of X-ray analysis but failed to find the presence of element No. 72 in the most soluble fractions of the rare earth elements of the yttria group examined by them. Arc spectrum analysis did, however, show the presence of this element in the double sulfate residues obtained from the soluble end fractions of various yttria earths.

Lee [14] has prepared a comprehensive list of minerals containing hafnium from various points of the globe and gives the estimated hafnium composition. He also calls attention to the suggested use

[8] Hopkins, *J. Franklin Inst.,* **204:** 1 (1927).
[9] Rolla and Fernandes, *Z. anorg. allgem. Chem.,* **160:** 190 (1927).
[10] Yntema, *J. Am. Chem. Soc.,* **46:** 37 (1924).
[11] Rolla and Fernandes, *Gazz. chim. ital.,* **57:** 704 (1927).
[12] Davey, *Phys. Rev.,* **25:** 882 (1925).
[13] Holton and Hopkins, *J. Am. Chem. Soc.,* **50:** 255 (1928).
[14] Lee, *Chemical Reviews,* **5:** 17 (1928).

of this element as a component of electric lamp filaments, particularly those used in radio tubes.

A patent has been issued to Coster and von Hevesy [15] for a method of separating hafnium and zirconium by the fractional crystallization of the oxychlorides or other halogen compounds from a solution of HCl; to VanArkel and deBoer [16] for a method of separation in which a mixture of compounds, such as the orthophosphates, is treated with hafnium and the resulting complex compounds are subjected to fractional crystallization; and to deBoer,[17] in which a solution is formed from the action of concentrated H_2SO_4 on a mixture of the phosphates of Hf and Zr to which at least one other salt of Hf and Zr is added and this mixture precipitated with water.

Zirconium. The literature of zirconium has been enriched by an article of deBoer [18] describing a method for the production of very pure ductile zirconium metal by the decomposition of tetraiodide vapor by means of a heated filament. He outlines a method of treatment starting with the ore and including methods for the purification of zirconium salts. He gives the melting point of the pure metal as 2130° K. and its specific gravity (free from hafnium) as 6.53. He also gives its electrical behavior and some high temperature measurements of interest and describes its chemical behavior with certain reagents. Reference is also made to some interesting zirconium alloys. Kiess [19] gives wave length measurements of the arc and the spark spectra of zirconium; he has photographed the spectra of the pure metal with concave grating and with quartz prism spectrographs. The measured wave lengths in the arc cover from 4881 AU in the blue to 9277 AU in the infra red, thus extending our spectra more than 2000 units beyond the longest wave length previously observed.

Davey [20] finds that ZrO_2 appears to crystallize in several forms, two of which have been studied by the powder method. One shows a face-centered cubic lattice and the second a triangular close packed lattice both of which give a density of 6.13. Binks [21] has studied the crystalline structure of zircon and finds it to resemble $CaSO_4$, the distribution of atoms about the c-axis being similar

[15] Coster and von Hevesy, U.S.P. 1666440 (Apr. 17, 1928).
[16] VanArkel and deBoer, U.S.P. 1666800 (Apr. 17, 1928).
[17] deBoer, U.S.P. 1666811 (Apr. 17, 1928).
[18] deBoer, *Ind. Eng. Chem.*, **19:** 1256 (1927).
[19] Kiess, Bur. Standards Sci. Papers, no. **548:** 47 (1927).
[20] Davey, *Phys. Rev.*, **27:** 798 (1926).
[21] Binks, *Mineralogical Mag.*, **21:** 176 (1926).

to that about the a-axis of anhydrite. This work confirms the in vestigations of Vegard. It was found by Dimbley, English, Firth, Hodkin and Turner [22] that up to 8% of ZrO_2 could be added to glasses without affecting the transparency and producing opalescence. The effects of the addition of ZrO_2 were increased viscosity and rate of setting, increase of annealing temperature, greater density, lowering thermal expansion and greater resistance to H_2O, HCl and alkalies.

Willetts [23] patents a zirconia-faced refractory material mainly formed of fire-clay but provided with a face of ZrO_2 which partially interpenetrates and is integrally united with the main body of the refractory article. The Corning Glass Works [24] describes a refractory article, in which ZrO_2 may be used, composed of crystals embedded in a glassy matrix and obtained by fusion, cast ing and annealing.

In the treatment of zirconia ores Kinzie [25] describes a method of heating with KOH, or other alkalies, to effect its decomposition and the treatment of the residue with some acid, like dilute H_2SO_4, to obtain the ZrO_2 and SiO_2 in acid solution. The precipitation of a zirconia compound is effected by cooling to $47°$; the SiO_2 remains in solution, while the precipitate is removed.

Reed and Withrow [26] report an interesting series of experiments undertaken by them to determine the possibility of using zirconium sulfate as an alternative test for the detection of potassium. The sensitiveness of this reagent has been determined under a variety of conditions of purity and concentration but the sodium cobaltic nitrite method is found to be somewhat more delicate.

Becket [27] describes a steel having a high shock resistance which contains Mn $1-2\%$, C less than 2% and Zr 0.15 to 0.50%. Fonda [28] describes a method of producing an alloy of zirconium and tungsten applicable to the production of filaments. A layer of Zr is formed on W by the thermal decomposition of zirconium chloride or other zirconium compound. The reaction is interrupted and the W and Zr are then heated to a higher temperature in an inert atmosphere to effect the alloying.

Allibone and Sykes [29] describe a series of alloys in which Zr

22 Dimbley, English, Firth, Hodkin and Turner, *J. Soc. Glass Tech.*, 11: 52 (1927).
23 Willetts, U.S.P. 1650577 (Nov. 22, 1927).
24 Corning Glass Works, Brit. P. 265847 (June 25, 1926).
25 Kinzie, U.S.P. 1658807 (Feb. 14, 1928).
26 Reed and Withrow, *J. Am. Chem. Soc.*, 50: 1515 (1928).
27 Becket, U.S.P. 1660409 (Feb. 28, 1928).
28 Fonda, U.S.P. 1658712 (Feb. 7, 1928).
29 Allibone and Sykes, *J. Inst. Metals*, 1928, no. 458. 14 p.

is alloyed with Cu and with Ni and also with Fe and give their hardness, tensile strength and ductility. In the case of Ni the Zr was introduced to the extent of 55% of the alloy; in the other cases to a somewhat lower limit. In each case the system is eutectiferous and intermediate compounds are formed.

Thorium. Further studies have been conducted on the function of thoria when used in connection with tungsten in the electric filament. Forsythe [30] finds the black body emissivity of ThO_2 to be 0.40 when heated either with oxy-hydrogen or oxy-gas flames. Dushman and Ewald [31] state that the electron emission of a monatomic layer of Th on W is best represented for zero field strength by the relation $I = 3T^2\varepsilon - 30,500/T$. They point out that the emission for a monatomic film of the Th on W is greater than that observed by metallic Th. Clansing [32] finds that Th moves outward in the coated wires along the W crystal interfaces, while diffusion through the intact W lattice takes place to a negligible degree, this being contrary to Langmuir's hypothesis. Geiss and van Liempt [33] state that ThO_2 in W filaments is reduced to the metal above 2700° abs. Th and W do not form mixed crystals and the diffusion of the ThO_2 towards the outside occurs along the edges of the grains of W and not through the lattice. In the course of his researches on high temperature equilibria and following his work on the high temperature equilibrium of ZrO_2 and C, Prescott [34] has measured the equilibrium between ThO_2 and C at temperatures from 2000 to 2500° K. and at pressures from two centimeters to two atmospheres. The increase in free energy and heat content attending this reaction at the above temperature range and at one atmosphere were found to be those given by the equations, $\Delta F° - 176,970 - 73.89T$ and $\Delta H - 176,970$ calories. At 2395° K. the free energy change becomes zero and the actual equilibrium pressure is one atmosphere.

Marden,[35] continuing his investigations on the production of rare metals in pure form, describes a method of production by which a salt of the rare metal, such as thorium ammonium chloride, is mixed with more than the theoretical quantity of metal, such as aluminium, required to reduce the salt. The mixture is heated to reduction temperature, other substances are separated

[30] Forsythe, *Phys. Rev.*, **25**: 252 (1925).
[31] Dushman and Ewald, *Phys. Rev.*, **29**: 857 (1927).
[32] Clansing, *Physica*, **7**: 193 (1927).
[33] Geiss and van Liempt, *Z. anorg. allgem. Chem.*, **168**: 107 (1927).
[34] Prescott, *J. Am. Chem. Soc.*, **48**: 2534 (1926).
[35] Marden, U.S.P. 1648954 (Nov. 15, 1927).

from the alloy formed by washing with water and the alloy is treated with HNO_3 or heated to volatilize the metal associated with the rare metal. Marden [36] also describes a method of manufacturing rare metal powders by heating with Mg and $CaCl_2$ or other fluxing agent.

Cerium. The study of cerium continues to be an attractive field of investigation in a number of research laboratories. Neckers and Kremers,[37] in developing a method of separating cerium from the other elements of the rare earth group, naturally found it necessary to bring this element to the ceric state. They have found it possible to produce an anodic oxidation of about 90% efficiency. No precipitation being effected, however, it was found necessary to add an ion, such as phosphate, which allows of an oxidation of about 99% efficiency and a resulting precipitation of the cerium.

Considerable attention has been given to the use of cerium as a reagent in volumetric analytical analyses. Martin [38] has determined hydrazoic acid by a method which depends upon its oxidation to nitrogen by ceric sulfate in acid solution. The method is said to be accurate to 0.1% if care is taken to eliminate the oxygen-iodine error and if the loss of hydrazoic acid by volatilization is prevented. Furman [39] finds that solutions of ceric sulfate in diluted sulfuric acid are sufficiently stable to be used in volumetric analyses. The reaction between ceric and ferrous solutions is suitable for the potentiometric determination of either ion with a high order of accuracy. Ceric solutions may be standardized or determined by titration with standard oxalic acid. The author recommends the use of pure ceric oxide in the preparation of the ceric salts. In another paper [40] Furman reports the potentiometric titration of vanadyl solutions with standard ceric sulfate to give accurate results, either in simple solutions or in the presence of large quantities of ferric and chromic salts. This method finds practical application in the direct determination of chromium in ferro alloys. Willard and Young,[41] in an extensive study of the same general subject, reach the conclusion that pure cerium is not essential and that the other associated rare earths do not interfere in oxidation-reduction reactions. They find that this reagent is in some cases a stronger oxidizing agent than is per-

[36] Marden, U.S.P. 1659209 (Feb. 14, 1928).
[37] Neckers and Kremers, *J. Am. Chem. Soc.*, **50**: 955 (1928).
[38] Martin, *J. Am Chem. Soc.*, **49**: 2133 (1927).
[39] Furman, *J. Am. Chem. Soc.*, **50**: 755 (1928).
[40] Furman, *J. Am. Chem. Soc.*, **50**: 1675 (1928).
[41] Willard and Young, *J. Am. Chem. Soc.*, **50**: 1322 (1928).

manganate in acid solution and has a number of advantages over the latter. Instead of operating at elevated temperatures they find that titration can be carried out at room temperature by the use of iodine chloride as a catalyst. The end point may be determined either electrometrically or with indicators. They have applied this method to the determination of ferrous iron and also of calcium. Continuing their investigations the same authors [42] have made a detailed study of the application of the ceric sulfate method to the titration of iron in iron ores following a stannous chloride reduction in hydrochloric acid or a reduction with aluminium or zinc in sulfuric acid solution. They find that arsenious acid does not interfere in this method. These same investigators [43] also report that iodine may be determined very accurately in a sulfuric acid solution by electrometric titration to iodine with standard ceric sulfate. Moderate amounts of bromine may be present. This method may be reversed and used successfully in the volumetric determination of cerium after a bismuthate oxidation. They also use ceric sulfate successfully [44] in the volumetric determination of arsenic and of antimony, potassium bromide or iodine chloride being used as a catalyst. Their further investigations [45] have resulted in the detailed development of a method for the volumetric determination of cerium in the presence of the other associated rare earths by oxidation with persulfate in the presence of silver nitrate as a catalyst, followed by electrometric titration with standard ferrous sulfate, potassium iodide or sodium nitrite. Great speed and accuracy is claimed for this method.

Miscellaneous. The fractional precipitation of the rare earths by electrolysis has been investigated by Neckers and Kremers,[46] who have found it possible to separate lanthanum from praseodymium and the other cerium group earths. The addition of 5% sodium chloride increases the conductivity and thus the rate of precipitation threefold without impairing the efficiency of the fractionation. Other separations in the cerium group were not found to be feasible. The authors have also investigated the solubility of the rare earth oxalates in nitric acid and in mixtures of nitric and oxalic acids. Kleinhecksel and Kremers [47] conducted an extensive investigation on anhydrous rare earth chlorides, determining

[42] Willard and Young, *J. Am. Chem. Soc.*, **50**: 1334 (1928).
[43] Willard and Young, *J. Am. Chem. Soc.*, **50**: 1368 (1928).
[44] Willard and Young, *J. Am. Chem. Soc.*, **50**: 1372 (1928).
[45] Willard and Young, *J. Am. Chem. Soc.*, **50**: 1379 (1928).
[46] Neckers and Kremers, *J. Am. Chem. Soc.*, **50**: 950 (1928).
[47] Kleinhecksel and Kremers, *J. Am. Chem. Soc.*, **50**: 959 (1928).

densities, melting points and hydrogen ion concentrations. The elements particularly studied were lanthanum, cerium, praseodymium, neodymium, samarium, dysprosium, yttrium, holmium and thulium.

Meggers [48] gives new data concerning the LaII spectra and Meggers and Burns [49] have examined several hundred La lines excited by a vacuum arc and made with a diffraction grating. Even these extensive data are said to be incomplete. Randall and Chang [50] have determined the solubility of thallous chloride not only in water and in magnesium sulfate but also in lanthanum nitrate solutions.

Boss and Hopkins [51] applied the fractional precipitation method with sodium nitrite to erbium-yttrium material from gadolinite and obtained erbium of the constant atomic weight of 167.64. Identical results were obtained by the nitrate fusion method.

Giauque [52] has made a valuable contribution to the study of paramagnetism and the third law of thermodynamics. The low temperature magnetic susceptibility data of gadolinium sulfate have been shown to agree quantitatively with an equation, using natural constants and based on orientation without restraint within the solid.

Wells [53] has made a careful study of the Smith method of analyzing samarskite, showing how the various elements distribute themselves in the treatment with hydrofluoric acid. He shows in another paper [54] that the credit for recognizing a new element in samarskite should be given to J. Lawrence Smith, although his preparations were impure and his characterization of "Mosandrum" indefinite. This supposed elementary substance was later found to be a mixture of samarium and gadolinium.

It is evident from the foregoing that American chemists have made substantial contributions to our knowledge of the rare earths during the past year. These have come from such varied sources that we may confidently anticipate a continuation of these researches and the publication of further results.

[48] Meggers, *J. Opt. Soc. Am.*, **14**: 191 (1927).
[49] Meggers and Burns, *J. Opt. Soc. Am.*, **14**: 449 (1927).
[50] Randall and Chang, *J. Am. Chem. Soc.*, **50**: 1535 (1928).
[51] Boss and Hopkins, *J. Am. Chem. Soc.*, **50**: 298 (1928).
[52] Giauque, *J. Am. Chem. Soc.*, **49**: 1870 (1927).
[53] Wells, *J. Am. Chem. Soc.*, **50**: 1017 (1928).
[54] Wells, *J. Wash. Acad. Sci.*, **17**: 385 (1927).

Chapter XIX.

Aliphatic Compounds.

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This field engages the attention of American chemists increasingly, 94 papers this year as against 70 last year. They are grouped as before.

Identification and Estimation. Hann and Jamieson [1] have prepared the 2-methyl-5-isopropylanilides of the fatty acids from lauric to lignoceric for the purpose of identification. These derivatives have definite melting points lying between 81° and 94°. Hill [2] has applied the method of Marvel, Gauerke and Hill [3] to a number of other alkyl halides and gives the melting points of the derivatives.

The detection and estimation of methanol have engaged the attention of Whaley [4] and Williams [5] of the U. S. Internal Revenue Bureau.

Cassar [6] has proposed a method for estimating isopropyl alcohol in the presence of acetone and of *sec.*-butyl alcohol in the presence of methyl ethyl ketone.

Lactic acid, so important biologically, has interested several chemists. Germuth [7] has studied its detection in the presence of other organic acids. Ronzoni and Wallen-Lawrence [8] propose a quantitative method for its estimation in the blood and Mc-Clellan [9] one applicable to blood and urine. Friedemann [10] determines it in sugar solutions which have been decomposed by alkali.

[1] Hann and Jamieson, *J. Am. Chem. Soc.*, **50**: 1442 (1928).
[2] Hill, *J. Am. Chem. Soc.*, **50**: 167 (1928).
[3] Marvel, Gauerke and Hill, *J. Am. Chem. Soc.*, **47**: 3009 (1925).
[4] Whaley, *Ind. Eng. Chem.*, **20**: 320 (1928).
[5] Williams, *Ind. Eng. Chem.*, **19**: 844 (1927).
[6] Cassar, *Ind. Eng. Chem.*, **19**: 1061 (1927).
[7] Germuth, *Ind. Eng. Chem.*, **19**: 852 (1927).
[8] Ronzoni and Wallen-Lawrence, *J. Biol. Chem.*, **74**: 363 (1927).
[9] McClellan, *J. Biol. Chem.*, **76**: 481 (1928).
[10] Friedemann, *J. Biol. Chem.*, **76**: 75 (1928).

Peterson and West [11] have a volumetric method based on the use of acetanhydride in the presence of pyridine for the estimation of hydroxyl groups in alcohols, sugars and other organic compounds. The Zeisel method for methoxyl has been modified by Eaton and West [12] and made applicable to ethoxyl groups and to certain sulfur compounds.

From long manufacturing experience, Mallinckrodt [13] gives the tests for impurities in ether.

Lyons [14] shows that thioglycolic acid gives an extremely delicate color test for iron (1 part in 10,000,000) and that it can be used for the quantitative estimation of ferrous and ferric iron.

Physical Properties of Organic Compounds. As usual there are many papers in this division but they touch only a small fraction of the organic compounds about which we need more knowledge. Perry [15] gives us the vapor pressure curve for methylene chloride. Dana, Burdick and Jenkins [16] have determined the vapor pressures, vapor densities and liquid densities of vinyl chloride at different temperatures, also the latent heat of vaporization. Parks and Barton [17] supply vapor pressure data on isopropyl and tertiary butyl carbinols from 0 to 90° and also heats of vaporization.

The coefficient of expansion of bromoform has been measured by Sherman and Sherman. [18] The solubility of barium butyrate in water has been studied by Wing, [19] who finds it to have a minimum at about 30°. The salt is anhydrous.

The preparation and properties of diethyleneglycol nitrate are given by Rinkenbach. [20] The solubility of paraffin wax in the pure hydrocarbons, n-pentane, n-hexane, n-heptane, n-octane and iso-decane, has been measured by Weber and Dunlap. [21]

Parks and Nelson [22] find the heat of vaporization of ethyl alcohol to be 208.7 and that of isopropyl alcohol to be 161.0 cal. per gram.

The dissociation constant of acetic acid has been determined by

[11] Peterson and West, *J. Biol. Chem.*, **74**: 379 (1927).
[12] Eaton and West, *J. Biol. Chem.*, **75**: 283 (1927).
[13] Mallinckrodt, *J. Am. Chem. Soc.*, **39**: 2655 (1927).
[14] Lyons, *J. Am. Chem. Soc.*, **49**: 1916 (1927).
[15] Perry, *J. Phys. Chem.*, **31**: 1737 (1927).
[16] Dana, Burdick and Jenkins, *J. Am. Chem. Soc.*, **49**: 2801 (1927).
[17] Parks and Barton, *J. Am. Chem. Soc.*, **50**: 24 (1928).
[18] Sherman and Sherman, *J. Am. Chem. Soc.*, **50**: 1119 (1928).
[19] Wing, *J. Am. Chem. Soc.*, **49**: 2859 (1927).
[20] Rinkenbach, *Ind. Eng. Chem.*, **19**: 925 (1927).
[21] Weber and Dunlap, *Ind. Eng. Chem.*, **20**: 383 (1928).
[22] Parks and Nelson, *J. Phys. Chem.*, **32**: 61 (1928).

Cohn, Heyroth and Menkin [23] and that of acetamide (as an acid) by Branch and Clayton.[24] They find its K to be 8×10^{-16}, which shows it to be an extremely weak acid.

The dielectric constants of carbon tetrachloride, methyl acetate, ethyl acetate, acetone, ethyl and isoamyl alcohols have been measured by Krchma and Williams.[25]

Francis [26] has found the free energies of methane, octane, ethane, ethylene and acetylene and of methyl, ethyl, propyl, butyl, isopropyl, isobutyl and *tert*.-butyl alcohols.

Smith, Boord, Adams and Pease [27] explain the presence of the benzene lines that were found in three previously published spectra of a number of aliphatic compounds.

Constitution and Composition of Natural Substances. Davies and Adams [28] have studied jalapinolic and convolvulinoic acids and have identified the former with d-11-hydroxyhexadecanoic acid.

By continued fractionation of 130 kilos of the methyl esters of coconut oil acids, Taylor and Clarke [29] have shown the composition to be 0.48% caproate, 8.9% caprylate, 5.7% caprate, 45.2% laurate, 16.5% myristate and 23.4% higher esters. The fat from the Kentucky coffee nut tree seed has been found by Barkenbus and Zimmerman [30] to contain 37.4% olein, 56.4% linolein, 5.07% palmitin and stearin and 1.28% unsaponifiable. Kerr [31] finds boa constrictor fat to contain an acid with four double bonds, along with linolic, oleic, palmitic and stearic acids. Calcium citrate is identified by Peterson, Wilson, McCoy and Fred [32] in cultures of butyric acid forming bacteria. This salt has 4 molecules of water and does not retain two of these at $110°$, as is stated in the literature.

Burrell [33] gives a comprehensive statement of our present knowledge of the composition of petroleum and its products.

Preparation of Compounds. The synthesis of methanol from carbon monoxide and hydrogen is thoroughly treated in a theoretical and experimental paper by Lewis and Frolich.[34] In another

23 Cohn, Heyroth and Menkin, *J. Am. Chem. Soc.*, **50**: 696 (1928).
24 Branch and Clayton, *J. Am. Chem. Soc.*, **50**: 1680 (1928).
25 Krchma and Williams, *J. Am. Chem. Soc.*, **49**: 2408 (1927).
26 Francis, *Ind. Eng. Chem.*, **20**: 277, 283 (1928).
27 Smith, Boord, Adams and Pease, *J. Am. Chem. Soc.*, **49**: 3137 (1927).
28 Davies and Adams, *J. Am. Chem. Soc.*, **50**: 1749 (1928).
29 Taylor and Clarke, *J. Am. Chem. Soc.*, **49**: 2829 (1927).
30 Barkenbus and Zimmerman, *J. Am. Chem. Soc.*, **49**: 2061 (1927).
31 Kerr, *J. Am. Chem. Soc.*, **49**: 2046 (1927).
32 Peterson, Wilson, McCoy and Fred, *J. Am. Chem. Soc.*, **49**: 2884 (1927).
33 Burrell, *Ind. Eng. Chem.*, **20**: 602 (1928).
34 Lewis and Frolich, *Ind. Eng. Chem.*, **20**: 285 (1928).

paper the same authors [35] consider the possibilities of obtaining higher alcohols from the same materials. Smith, Davis and Reynolds [36] discuss the synthesis of higher hydrocarbons from water gas.

Lind and Glockler [37] have ascertained the conditions under which liquid hydrocarbons may be obtained by passing an electric discharge through ethane. The methods of preparation and physical properties of *n*-butane, isobutane and the three butylenes are given by Coffin and Maass. [38]

A promising synthetic method by which an alcohol is lengthened by three carbons at a time is described by Rossander and Marvel. [39]

Dillon and Lucas [40] describe the preparation of 3- and 4-heptanols and the corresponding bromoheptanes.

Davis and Elderfield [41] obtain a 32.5% yield of methylamine by passing methanol and ammonia over thoria. The preparation and properties of halogenated tertiary amines, such as $BrCH_2CH_2$-$CH_2N(C_2H_5)_2$ and $BrCH_2CH_2CH_2CH_2N(C_2H_5)_2$, are described by Marvel, Zartman and Bluthardt. [42] Alkyl-amino-ethanol and propanol are discussed by Pierce. [43]

A new method of obtaining O,N-dialkyl-hydroxylamines has been devised by Major and Fleck. [44]

Sah [45] has devised a new method for preparing esters of ortho-acetic acid by which the mixed as well as the simple esters may be obtained.

The preparation of acid chlorides by means of thionyl chloride has been made more reliable by the study of McMaster and Ahmann. [46] Montonna [47] finds that silicon tetrachloride reacts with acids to give good yields of the acid chlorides, up to 85% with acetic acid. From the sodium salt the acid anhydride is obtained.

The mercapto group has been introduced in the alpha-position into caproic, lauric, myristic, palmitic and stearic acids by Nicolet and Bate. [48]

[35] Lewis and Frolich, *Ind. Eng. Chem.*, **20**: 354 (1928).
[36] Smith, Davis and Reynolds, *Ind. Eng. Chem.*, **20**: 462 (1928).
[37] Lind and Glockler, *J. Am. Chem. Soc.*, **50**: 1767 (1928).
[38] Coffin and Maass, *J. Am. Chem. Soc.*, **50**: 1427 (1928).
[39] Rossander and Marvel, *J. Am. Chem. Soc.*, **50**: 1491 (1928).
[40] Dillon and Lucas, *J. Am. Chem. Soc.*, **50**: 1711 (1928).
[41] Davis and Elderfield, *J. Am. Chem. Soc.*, **50**: 1786 (1928).
[42] Marvel, Zartman and Bluthardt, *J. Am. Chem. Soc.*, **49**: 2299 (1927).
[43] Pierce, *J. Am. Chem. Soc.*, **50**: 241 (1928).
[44] Major and Fleck, *J. Am. Chem. Soc.*, **50**: 1479 (1928).
[45] Sah, *J. Am. Chem. Soc.*, **50**: 516 (1928).
[46] McMaster and Ahmann, *J. Am. Chem. Soc.*, **50**: 145 (1928).
[47] Montonna, *J. Am. Chem. Soc.*, **49**: 2114 (1927).
[48] Nicolet and Bate, *J. Am. Chem.*, **49**: 2065 (1927).

A synthesis of α,β,γ-trimethylglutaric acid has been worked out by Ray.[49]

The preparation of glycine has been improved by Robertson.[50] The preparation and purification of arginine and histidine have been investigated by Vickery and Leavenworth.[51]

A method for obtaining lignin from corn cobs has been worked out by Phillips.[52]

Peterson and Spencer [53] give a preparation method for cellobiose.

Reactions of Compounds. The dissociation of ethane, propane, butane and isobutane at 650° has been studied by Pease.[54] Butane, for instance, breaks up in two ways:

$$C_4H_{10} \rightarrow C_3H_6 + CH_4 \text{—demethanation}$$
$$C_4H_{10} \rightarrow C_4H_8 + H_2 \text{—dehydrogenation}$$

Demethanation increases with the complexity of the hydrocarbon, while dehydrogenation remains nearly the same.

Norris and Reuter [55] have investigated the rearrangements which certain hydrocarbons undergo. Isopropylethylene changes into trimethylethylene under the influence of alumina, phosphoric acid and aluminum sulfate. The reverse change does not take place. Guest [56] has studied the rearrangement in vapor phase of alkyl acetylenes. Under the influence of heat $RC : CH \rightarrow R'C : CR''$. This is reversed by treatment with sodamide.

The catalytic reactions of ethylene have been investigated by Walker.[57] Under the influence of iron it polymerizes completely at 360° to a colorless oil. Ethylene is found by Rea and Mullinix [58] to aid in the transformation of starch into sugar. Bruson and Calvert [59] find that nascent thiocyanogen adds to isoprene and dimethylbutadiene at 5° to give crystalline compounds melting at 76 and 130°.

The liquid alloy of sodium and potassium has been found by Conant and Blatt [60] to react with petroleum hydrocarbons to give highly colored metallic derivatives, which react with carbon di-

[49] Ray, *J. Am. Chem. Soc.*, **50**: 558 (1928).
[50] Robertson, *J. Am. Chem. Soc.*, **49**: 2889 (1927).
[51] Vickery and Leavenworth, *J. Biol. Chem.*, **75**: 115 (1927); **76**: 701 (1928).
[52] Phillips, *J. Am. Chem. Soc.*, **49**: 2037 (1927).
[53] Peterson and Spencer, *J. Am. Chem. Soc.*, **49**: 2822 (1927).
[54] Pease, *J. Am. Chem. Soc.*, **50**: 1779 (1928).
[55] Norris and Reuter, *J. Am. Chem. Soc.*, **49**: 2624 (1927).
[56] Guest, *J. Am. Chem. Soc.*, **50**: 1744 (1928).
[57] Walker, *J. Phys. Chem.*, **31**: 961 (1927).
[58] Rea and Mullinix, *J. Am. Chem. Soc.*, **49**: 2116 (1927).
[59] Bruson and Calvert, *J. Am. Chem. Soc.*, **50**: 1735 (1928).
[60] Conant and Blatt, *J. Am. Chem. Soc.*, **50**: 542 (1928).

oxide to form salts of acids. The polymerization of unsaturated hydrocarbons by sulfuric acid has been studied by Morrell.[61]

Fry and Otto and Fry and Schulze [62] have made an extensive study of the action of fused caustic alkalies on alcohols, poly-alcohols and the sugars. In all cases the alkali carbonates are formed and hydrogen and the simpler hydrocarbons are eliminated.

The saponification coefficient of ethyl acetate has been determined with great accuracy by Terry and Stieglitz.[63]

Acetoacetic ester has been condensed with glucose by West.[64]

Nicolet and Potts [65] find the rate of the reaction of isopropyl iodide with mercuric chloride to be proportional to the product of the concentration of the reactants and of the mercuric iodide formed.

The reactions of urethanes with ammonia and amines have been studied by Basterfield, Woods and Whelen.[66] Levulinic acid is found by Bennett [67] to form a ketazine but not a hydrazone.

The drying of oils is scientifically interesting and commercially important. The effect of oils from other seeds on the rate of drying has been studied by Eastman and Taylor.[68] Long, Egge and Wetterau [69] have considered the action of heat and of blowing on linseed and other oils. Long and Moore [70] have tried the effect of cathode rays on linseed oil. Stutz [71] has studied the absorption of ultraviolet light by drying oils containing driers.

The reactions of hydrogen sulfide with amino- and imino-nitriles have been investigated by Gatewood and Johnson.[72]

The successive steps in the chlorination of 2.2'-dichloroethyl sulfide have been elucidated by Lawson and Dawson.[73] The thermal decomposition of organic sulfur compounds, particularly the lower alkyl disulfides, has been studied by Faragher, Morrell and Comay.[74] Wood and Travis [75] find that sodium hypochlorite converts a number of alkyl sulfides to sulfones.

[61] Morrell, *Ind. Eng. Chem.*, **19**: 794 (1928).
[62] Fry and Otto, *J. Am. Chem. Soc.*, **50**: 1122, 1138 (1928); Fry and Schulze, *ibid.*, 1131 (1928).
[63] Terry and Stieglitz, *J. Am. Chem. Soc.*, **49**: 2216 (1927).
[64] West, *J. Biol. Chem.*, **74**: 561 (1927).
[65] Nicolet and Potts, *J. Am. Chem. Soc.*, **50**: 212 (1928).
[66] Basterfield, Woods and Whelen, *J. Am. Chem. Soc.*, **49**: 2942 (1927).
[67] Bennett, *J. Am. Chem. Soc.*, **50**: 1747 (1928).
[68] Eastman and Taylor, *Ind. Eng. Chem.*, **19**: 896 (1927).
[69] Long, Egge and Wetterau, *Ind. Eng. Chem.*, **19**: 903 (1927).
[70] Long and Moore, *Ind. Eng. Chem.*, **19**: 901 (1927).
[71] Stutz, *Ind. Eng. Chem.*, **19**: 897 (1927).
[72] Gatewood and Johnson, *J. Am. Chem. Soc.*, **50**: 1422 (1928).
[73] Lawson and Dawson, *J. Am. Chem. Soc.*, **49**: 3119, 3125 (1927).
[74] Faragher, Morrell and Comay, *Ind. Eng. Chem.*, **20**: 527 (1928).
[75] Wood and Travis, *J. Am. Chem. Soc.*, **50**: 1226 (1928).

Constitution and Properties. Norris and Cortese [76] have continued their measurements on the reaction rates of alcohols with *p*-nitrobenzoyl chloride. Experiments with additional alcohols strengthen their conclusions as to the effect of structure of the alcohols on their reactivity. Allison and Hixon [77] have measured the heat of replacement of hydrogen by sodium for a large number of alcohols. For primary alcohols the average is 32.00, for secondary 29.75 and for tertiary 27.89 cal. per mole as compared with 31.87 for water.

Williams, Gabriel and Andrews [78] find a relation between the hydrolysis constants for esters and the strengths of the corresponding acids.

Street and Adkins [79] have studied the effect of the constitution of the alcohol and Carswell and Adkins, [80] the effect of the structure of the ketone, on rate of acetal formation.

Nicolet and Stevens [81] have compared the alcoholysis and hydrolysis rates of propyl and isopropyl iodides. In neutral solution the iso reacts much more rapidly than the normal but the reverse is the case in alkaline.

Knauss and Smull [82] have studied rates of addition of bromine to unsaturated acids to find evidence of stereoisomerism.

Dimethylaminoethyl esters of unsaturated acids are found by Gilman, Heckert and McCracken [83] to have local anæsthetic action.

Theory of Organic Reactions. Adkins and Broderick [84] find evidence of the union of alcohols with aldehydes to form what are probably hemiacetals, which may be regarded as the intermediate products in acetal formation.

Ramsperger [85] finds the decomposition of azoisopropane between 250 and 290° and 0.25 and 46 mm. to be a homogeneous unimolecular reaction. The heat of activation is calculated to be 40,900 cal. per mole.

Corson, Hazen and Thomas [86] conclude that enolization of aldehydes and ketones is not involved in their reactions with substances containing active hydrogen.

[76] Norris and Cortese, *J. Am. Chem. Soc.*, **49**: 2640 (1927).
[77] Allison and Hixon, *J. Am. Chem. Soc.*, **50**: 168 (1928).
[78] Williams, Gabriel and Andrews, *J. Am. Chem. Soc.*, **50**: 1267 (1928).
[79] Street and Adkins *J. Am. Chem. Soc.*, **50**: 162 (1928).
[80] Carswell and Adkins, *J. Am. Chem. Soc.*, **50**: 235 (1928).
[81] Nicolet and Stevens, *J. Am. Chem. Soc.*, **50**: 135 (1928).
[82] Knauss and Smull, *J. Am. Chem. Soc.*, **49**: 2808 (1927).
[83] Gilman, Heckert and McCracken, *J. Am. Chem. Soc.*, **50**: 437 (1928).
[84] Adkins and Broderick *J. Am. Chem. Soc.*, **50**: 499 (1928).
[85] Ramsperger, *J. Am. Chem. Soc.*, **50**: 714 (1928).
[86] Corson, Hazen and Thomas, *J. Am. Chem. Soc.*, **50**: 913 (1928).

The mechanism of the cleavage of diethyl α,α'-dibromoadipate by excess of diethylamine has been studied by Fuson.[87]

Gooch[88] has made a careful comparison of the rates of hydrolysis of ethyl acetate in the light and in the dark and finds no difference.

Smith[89] has calculated the equilibrium conditions for the formation of hydrocarbons and of alcohols from water gas. Salzberg and Marvel[90] have prepared hexa-*tert*-butylethynyl-ethane $[(CH_3)_3C.C\ C]_3C.C[C:C.C(CH_3)_3]_3$ as an analog of triphenylmethyl. It is undissociated in solution but rearranges at high temperature.

SUGGESTED RESEARCH

Each investigation of the past year should be studied for suggestions for further work. Aliphatic chemistry is particularly in need of consolidation : the facts that are now known need correlation. As this progresses the places where data are lacking will appear. The reactions of aliphatic compounds are not nearly as well understood as are those of the aromatic ; even the simplest reaction will repay thorough study.

RESEARCH BY INSTITUTIONS

Universities and Colleges	Types of Compounds	Investigators
California	Acetamide	G. E. K. Branch
		J. O. Clayton
	Glycine	G. Ross Robertson
	Bromoform	Albert Sherman
		Jack Sherman
California Inst. Tech......	Heptanols	R. T. Dillon
		H. J. Lucas
Carthage	Alkyl halides	E. L. Hill
Chicago	Ethyl acetate	Julius Stieglitz
		Ethel Terry
		W. T. Gooch
	Alkyl halides	B. H. Nicolet
		W. McD. Potts
		D. R. Stephens
	Mercapto acids	B. H. Nicolet
		L. F. Bate
Cincinnati	Alcohols	H. S. Fry
		Earl Otto
		Else L. Schulze

[87] Fuson, *J. Am. Chem. Soc.,* **50**: 1444 (1928).
[88] Gooch, *J. Am. Chem. Soc.,* **49**: 2257 (1927).
[89] Smith, *Ind. Eng. Chem.,* **19**: 801 (1928).
[90] Salzberg and Marvel, *J. Am. Chem. Soc.,* **50**: 1737 (1928).

Universities and Colleges	Types of Compounds	Investigators
Cornell	Ethylene	H. W. Walker
Georgetown	Amino alcohols	J. S. Pierce
Harvard	Hydrocarbons	J. B. Conant
		A. H. Blatt
	Acetic acid	E. J. Cohn
		F. F. Heyroth
		Miriam M. F. Menkin
Illinois	Adipic acid	R. C. Fuson
	Levulinic acid	C. W. Bennett
	Alcohols	C. S. Marvel
		S. S. Rosander
		O. D. Bluthardt
	Trimethylglutaric acid	F. E. Ray
	Jalapinolic acid	Roger Adams
		Letha Davis
	Free radicals	P. L. Salzberg
		C. S. Marvel
Iowa State	Alkylaminoesters	Henry Gilman
		L. C. Heckert
		R. McCracken
	Alcohols	J. B. Allison
		R. M. Hixon
Kentucky	Fats	Charles Barkenbus
		A. J. Zimmerman
Lehigh	Drying oils	J. S. Long
		G. N. Moore
		P. C. Wetterau
	Unsaturated acids	C. A. Knauss
		J. G. Smull
Mass. Inst. Tech..........	Alcohols	J. F. Norris
		Frank Cortese
	Hydrocarbons	J. F. Norris
		Raymond Reuter
	Alcohols	W. K. Lewis
		P. K. Frolich
	Methylamine	T. L. Davis
		R. C. Elderfield
McGill	Hydrocarbons	C. C. Coffin
		O. Maass
Middlebury	Keto-enols	B. B. Corson
		R. K. Hazen
		J. S. Thomas
Mississippi College	Sulfides	A. E. Wood
		E. G. Travis
Minnesota	Ethane	S. C. Lind
		G. Glockler
N. Y. State Col. Forestry..	Cellobiose	F. C. Peterson
		C. C. Spencer
Ohio State	Ultraviolet absorp.	C. E. Boord
		A. W. Smith
		C. S. Adams
		C. S. Pease

RESEARCH BY INSTITUTIONS—*Continued*

Universities and Colleges	Types of Compounds	Investigators
Oregon	Esterification	R. J. Williams A. Gabriel R. C. Andrews
Princeton	Hydrocarbons Hydroxylamines	R. N. Pease R. T. Major E. E. Fleck
Rockford	Ethylene	Helen E. Rea R. D. Mullinix
Saskatchewan	Urethanes	S. Basterfield E. L. Woods M. S. Whelen
School Mines, Mo.........	Hydrocarbons	Paul Weber H. L. Dunlap
S. Dakota State...........	Butyric acid	H. J. Wing
Stanford	Azoisopropane Alcohols	H. C. Ramsperger G. S. Parks Bernard Barton W. K. Nelson
Washington Sch. Med.....	Acetoacetic ester Hydroxyl esters	E. S. West E. S. West V. L. Patterson
	Methoxyl esters	E. S. West Emily P. Eaton
	Lactic acid	T. E. Friedemann Ethel Ronzoni Zonja Wallen-Lawrence
Washington Univ.	Acid chlorides	L. McMaster F. F. Ahmann
Wisconsin	Acetals	Homer Adkins H. E. Carswell J. N. Street A. E. Broderick
	Orthoacetates Citric acid	Peter P. T. Sah W. H. Peterson P. W. Wilson Elizabeth McCoy
Yale	Aminonitriles	T. B. Johnson Elizabeth Gatewood
	Acid chlorides	R. E. Montonna

Research Institutes, etc.

Bellevue Hospital, N. Y...	Dihydroxyacetone	W. S. McClellan
Bur. Animal Husbandry ..	Fats	R. K. Kerr
Bur. Chem. and Soils	Fatty acids	R. M. Hann G. S. Jamieson
Bureau of Mines..........	Hydrocarbons and alcohols	D. F. Smith J. D. Davis D. A. Reynolds
	Diethyleneglycol	W. H. Rinkenbach
Color Laboratory	Lignin	Max Phillips
Conn. Ag. Ex. St.........	Arginine	H. B. Vickery C. S. Leavenworth

Research by Institutions—*Continued*

Research Institutes, etc.	Types of Compounds	Investigators
Edgewood Arsenal	Mustard gas	W. E. Lawson
		T. P. Dawson
Internal Revenue Bur.	Methanol	John F. Williams
		Wm. L. O. Whaley
Public Works, Baltimore..	Lactic acid	F. G. Germuth

Industrial Laboratories

Eastman Kodak Co........	Coconut oil	H. T. Clarke
		E. R. Taylor
William O. Goodrich Co...	Drying oils	W. H. Eastman
		W. L. Taylor
Goodyear T. & R. Co.....	Butadiene	H. A. Bruson
		W. A. Calvert
Linde Air Products Co....	Vinyl chloride	L. I. Dana
		J. N. Burdick
		A. C. Jenkins
Arthur D. Little, Inc......	Hydrocarbons	A. W. Francis
	Alcohols	A. W. Francis
Mallinckrodt Ch. Wks. ...	Ether	E. Mallinckrodt, Jr.
N. J. Zinc Co.............	Drying oils	G. F. A. Stutz
Parke, Davis & Co........	Thioglycolic acid	Edward Lyons
Standard Oil Co., N. J.....	Alcohols	H. A. Cassar
Universal Oil Products Co.	Hydrocarbons	J. C. Morrell
	Sulfur compounds	W. F. Faragher
		J. C. Morrell
		S. Comay
J. B. Williams Co.........	Acetylene derivatives	H. H. Guest

Chapter XX.

Carbocyclic Series.

By C. S. Marvel,

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In this review of the past year's work in the carbocyclic series many of the papers which deal with carbon rings are not included; the discussion of numerous articles is omitted because the investigations fall more naturally into fields covered by other chapters. There has always been some question concerning the proper place for papers treating of compounds with carbon rings attached to aliphatic chains; all such papers have been omitted from this review where the reactions and properties described are clearly those of the aliphatic part of the molecule.

Alicyclic Compounds. The amount of work on the cyclo-paraffins seems to be increasing and a number of interesting papers have appeared in this field. Nicolet and Sattler [1] have obtained evidence that the opening of the cyclopropane ring by bromine proceeds in two steps. First the bromine replaces a hydrogen in the ring to give a bromocyclopropane derivative and hydrogen bromide and then the brominated cyclopropane ring is opened by the action of the hydrogen bromide. Kohler [2] has isolated and characterized two new stereoisomerides of the previously known benzoylphenylnitrocyclopropane. Kohler and Allen [3] have obtained two of the four possible stereoisomeric forms of

$$C_6H_5-\overset{3}{C}H$$
$$\overset{1}{\underset{2}{|}}\!\!>\!\overset{1}{C}HCOC_6H_4OCH_3$$
$$C_6H_5-\overset{2}{C}NO_2$$
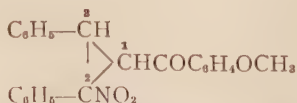
and have studied their behavior toward bases. One isomer opens

[1] Nicolet and Sattler, *J. Am. Chem. Soc.,* **49**: 2066 (1927).
[2] Kohler, *J. Am. Chem. Soc.,* **50**: 221 (1928).
[3] Kohler and Allen, *J. Am. Chem. Soc.,* **50**: 884 (1928).

between carbons 2 and 3 to give $C_6H_5CH = C - COC_6H_4OCH_3$

$$|$$
$$C_6H_5CHNO_2$$

and the other isomer opens between carbons 1 and 2 to give

$$C_6H_5-C = C-CH_2COC_6H_4OCH_3.$$
$$| \quad |$$
$$OCH_3 \ C_6H_5$$
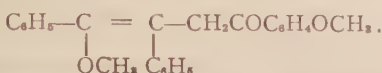
This shows that the action of alkali on these nitrocyclopropane derivatives depends to a remarkable degree upon their configuration. West[4] has reported on a condensation product of glucose and ethyl acetoacetate which he believes may contain a cyclopropane ring. Bateman and Marvel[5] have confirmed the findings of Ramart[6] that the hydrocarbon obtained by the dehydration of diphenyl-*tert*.-butyl carbinol is not a cyclopropane derivative.

Fuson[7] has studied the mechanism of the cleavage of diethyl α,α'-dibromoadipate by diethylamine previously observed by von Braun, Leistner and Münch.[8] The new results indicate the presence of a cyclobutane derivative as an intermediate product in this unusual reaction.

The investigation of substances related to chaulmoogric acid has been continued. Arvin and Adams[9] have prepared cyclopentenyl derivatives of the type

$$CH = CH$$
$$| \qquad > CH-CH-R.$$
$$CH_2-CH_2 \qquad |$$
$$\qquad\qquad CO_2H$$
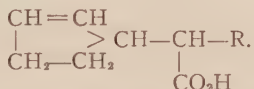
Yohe and Adams[10] have described cyclopentyl derivatives of a similar type and also those with three methylene groups between the ring and the carboxyl group. Adams, Stanley, Ford and Peterson[11] have described cyclohexylalkyl alkyl acetic acids of the type $C_6H_{11}(CH_2)_xCH(CO_2H)R$, where x is 2 to 4. Adams, Stanley and Stearns[12] have studied cyclohexyl and cyclohexylmethyl alkyl acetic acids. In all of these different types of compounds the molecular weight of an acid seemed to be the best index of its bactericidal action toward *B. Leprae*. All of the acids

4 West, *J. Biol. Chem.*, **74**: 561 (1927).
5 Bateman and Marvel, *J. Am. Chem. Soc.*, **49**: 2914 (1927).
6 Ramart, *Compt. rend.*, **179**: 634 (1924).
7 Fuson, *J. Am. Chem. Soc.*, **50**: 1444 (1928).
8 von Braun, Leistner and Münch, *Ber.*, **59B**: 1950 (1926).
9 Arvin and Adams, *J. Am. Chem. Soc.*, **49**: 2940 (1927).
10 Yohe and Adams, *J. Am. Chem. Soc.*, **50**: 1503 (1928).
11 Adams,, Stanley, Ford and Peterson, *J. Am. Chem. Soc.*, **49**: 2934 (1927).
12 Adams, Stanley and Stearns, *J. Am. Chem. Soc.*, **50**: 1475 (1928).

containing a total of sixteen to eighteen carbon atoms were effective bactericides toward this organism.

Perkins, Cruz and Reyes [13] have published the details for the isolation of hydnocarpic acid from a number of different oils. Santiago and West [14] have prepared certain new amides of chaulmoogric acid.

Stephens [15] has studied the oxidation of cyclohexene by air and has described a liquid peroxide which he has isolated in a pure condition. This peroxide has been shown to have the simple formula $C_6H_{10}O_2$. It has a tendency to polymerize to a molecule of twice the size which still retains the peroxide properties.

Two publications on the cyclic terpenes have appeared. Adams and Billinghurst [16] have reported the constants of the essential oils in certain desert plants. Blum [17] has patented the preparation of borneol esters by the addition of *o*-benzoylbenzoic and *o*-naphthoylbenzoic acids to pinene.

Aromatic Compounds. The use of an olefine instead of the usual alkyl halide in the Friedel and Crafts' reaction has been further investigated by Berry and Reid.[18] Cline and Reid [19] have studied the derivatives of ethylbenzene and Copenhaver and Reid [20] have studied *m*-diethylbenzene, two hydrocarbons which are isolated rather readily from the products of the reaction of ethylene and benzene in the presence of aluminum chloride.

The mechanism of the Würtz synthesis has been investigated by Bachmann and Clarke.[21] The products of the action of sodium on chlorobenzene are easily explained by assuming intermediate formation of free phenyl radicals. Heptyl bromide was also studied and the products were found to be those that would be predicted if heptyl radicals were formed. The effects of liquid sodium-potassium alloys and liquid sodium amalgams on dixanthyls,[22] hexa- and tetra-arylated ethanes,[23] diaryl dialkyl ethanes and substituted styrenes [24] have been studied by Conant and his students. By use of these alkali alloys it is possible to differentiate

[13] Perkins, Cruz and Reyes, *Ind. Eng. Chem.*, **19**: 939 (1927).
[14] Santiago and West, *Philippine J. Sci.*, **33**: 265 (1927).
[15] Stephens, *J. Am. Chem. Soc.*, **50**: 568 (1928).
[16] Adams and Billinghurst, *J. Am. Chem. Soc.*, **49**: 2895 (1927).
[17] Blum, U.S.P. 1640639 (Aug. 30, 1927).
[18] Berry and Reid, *J. Am. Chem. Soc.*, **49**: 3142 (1927).
[19] Cline and Reid, *J. Am. Chem.*, **49**: 3150 (1927).
[20] Copenhaver and Reid, *J. Am. Chem. Soc.*, **49**: 3157 (1927).
[21] Bachmann and Clarke, *J. Am. Chem. Soc.*, **49**: 2089 (1927).
[22] Conant and Garvey, *J. Am. Chem. Soc.*, **49**: 2080 (1927).
[23] Conant and Garvey, *J. Am. Chem. Soc.*, **49**: 2599 (1927).
[24] Conant and Blatt, *J. Am. Chem. Soc.*, **50**: 551 (1928).

between certain compounds which contain reactive carbon-carbon linkages. Rogers and Dougherty have studied the structure of the addition products of hexaphenylethane and alkyl sulfides.[25]

The aromatic halogen compounds have received particular attention during the last year. A series of papers by Nicolet and his students [26] dealing with positive halogen in the benzene ring have appeared. The halogens in *o*- and *p*-halogenated amines, phenols and naphthols and in iodomesitylene are easily removed from the ring by the action of boiling hydrochloric acid. The rate of removal of halogens from halogenated phenols and naphthols increases with increase in hydrogen ion concentration. No similar production of positive halogen could be obtained by *m*-substitution with such groups as the nitro group. This has led to the view that a quinoid form of the molecule may be the active form.

The replacement of aromatic halogen by amino and phenolic groups has received considerable study. Hale and Britton [27] have published the details of the research which led to a commercial preparation of phenol from chlorobenzene, which was reported in the patent literature a year earlier. Weston and Adkins [28] have made a thorough study of the effect of catalysts on the reaction between bromobenzene and *N*-acetyl-*p*-toluidine and potassium phenoxide. The replacement of halogen by amino or hydroxyl groups in the benzoylbenzoic acids and in the anthraquinones has been the subject of several patents.[29] The removal of halogen from halogenated aromatic sulfonic acids by catalytic reduction with a nickel catalyst has also been patented.[30]

Improved methods of preparing several halogenated aromatic compounds have been reported. Lucas and Scudder [31] have described the preparation of 2-bromo-*p*-cresol from *p*-nitrotoluene. Blicke and Smith [32] have improved the preparation of *p*-iodoanisole. Johnson and Gauerke [33] have given the details for the preparation of *m*-bromonitrobenzene. Heisig [34] has described many

[25] Rogers and Dougherty, *J. Am. Chem. Soc.*, **50**: 149 (1928).
[26] Nicolet and Sampey, *J. Am. Chem. Soc.*, **49**: 1796 (1927); Nicolet and Ray, *J. Am. Chem. Soc.*, **49**: 1801 (1927); Nicolet and Sandin, *J. Am. Chem. Soc.*, **49**: 1806 (1927); Nicolet, *J. Am. Chem. Soc.*, **49**: 1810 (1927); Sampey, *J. Am. Chem. Soc.*, **49**: 2849, 2853 (1927).
[27] Hale and Britton, *Ind. Eng. Chem.*, **20**: 114 (1928).
[28] Weston and Adkins, *J. Am. Chem. Soc.*, **50**: 859 (1928).
[29] Gubelmann, Weiland and Stallmann, U.S.P. 1654287; 1654289 (Dec. 27, 1927); Gubelmann, U.S.P. 1654290 (Dec. 27, 1927); Thomas and Davies, U.S.P. 1657420 (Jan. 24, 1928).
[30] Schöllkopf, U.S.P. 1645974 (Oct. 18, 1927).
[31] Lucas and Scudder, *J. Am. Chem. Soc.*, **50**: 244 (1928).
[32] Blicke and Smith, *J. Am. Chem. Soc.*, **50**: 1229 (1928).
[33] Johnson and Gauerke, *Organic Syntheses*, **8**: 46 (1928).
[34] Heisig, *J. Am. Chem. Soc.*, **50**: 139 (1928).

new polyhalogen compounds in his study of the melting points of halogenated benzene derivatives. Gubelmann, Weiland and Stallmann [35] have devised a method for separating 3,4-dichloroaniline from a mixture of dichloroanilines. An improved procedure for the analysis of brominated cresols has been described by Buxton and Lucas.[36]

The work stimulated by the discovery of the germicial properties of hexyl resorcinol has been continued and several papers and patents on related products have appeared during the last year. Talbot and Adams [37] have prepared cyclohexyl-, β-cyclohexylethyl- and cyclopentylmethylresorcinol and have found that they are all less effective germicides than hexylresorcinol. Bartlett and Garland [38] have also described cyclohexylresorcinol and numerous cyclohexyl derivatives of phenol and phenol ethers. Phillips [39] has patented the preparation of cyclohexylresorcinol by the condensation of cyclohexanol and resorcinol in the presence of zinc chloride. Dohme [40] has patented the preparation of numerous alkyl resorcinol derivatives.

The optimum conditions for the fusion of sodium benzenesulfonate with alkalies to produce phenol have been determined by Rhodes, Jayne and Bivins.[41] Small amounts of phenols have been isolated from crude petroleums and larger amounts from cracked petroleum by Story and Snow.[42] They have definitely identified a few of the phenols.

The rearrangements of the acyl derivatives of o-aminophenol have been studied further during the last year. Nelson, Shock, and Sowers [43] and Nelson, Matchett and Tindall [44] have contributed to this study. Raiford and Mortensen [45] have studied acyl derivatives of o-aminocyclohexanol and of α-aminobenzyl-2-naphthol and have found that no rearrangement occurs in these compounds.

Brubaker and Adams [46] have made an extensive study of the condensation products of opianic acid and of o-phthalaldehydic acid with phenol and various of its derivatives. This study has cleared up many of the structure problems in this field.

[35] Gubelmann, Weiland and Stallmann, U.S.P. 1663251 (March 20, 1928).
[36] Buxton and Lucas, J. Am. Chem. Soc., 50: 249 (1928).
[37] Talbot and Adams, J. Am. Chem. Soc., 49: 2040 (1928).
[38] Bartlett and Garland, J. Am. Chem. Soc., 49: 2098 (1927).
[39] Phillips, U.S.P. 1650036 (Nov. 22, 1927).
[40] Dohme, U.S.P. 1649667; 1649668; 1649669; 1649670 (Nov. 15, 1927).
[41] Rhodes, Jayne and Bivins, Ind. Eng. Chem., 19: 804 (1927).
[42] Story and Snow, Ind. Eng. Chem., 20: 359 (1928).
[43] Nelson, Shock and Sowers, J. Am. Chem. Soc., 49: 3129 (1927).
[44] Nelson, Matchett and Tindall, J. Am. Chem. Soc., 50: 919 (1928).
[45] Raiford and Mortensen, J. Am. Chem. Soc., 50: 1201 (1928).
[46] Brubaker and Adams, J. Am. Chem. Soc., 49: 2279 (1927).

The oxidation of aromatic compounds has been discussed in several papers. Hellerman [47] and Hellerman and Sanders [48] have prepared β-triphenylethylamine and diphenylmethylamine and have investigated the oxidation of the latter compound. Stephens [49] has reported on the oxidation of certain α-phenyl carbinols with gaseous oxygen. Gardner [50] has studied the oxidation of α-nitronaphthalene in alkaline solution and has found that the ring containing the nitro groups is oxidized under these conditions. Several patents [51] concerning catalytic oxidation of hydrocarbons to more unsaturated hydrocarbons or to aldehyde or ketone derivatives have also appeared during the last year.

Some contributions to the subject of nitration and the reduction of nitro compounds have been made. Pinck [52] has obtained very good yields of nitro compounds by the action of nitrogen tetroxide on aromatic hydrocarbons. Wheeler and Brooks [53] have studied the nitration of 2-aminocymene. Two patents on the nitration of benzene have been recorded. Livingston and Kyrides [54] have used special conditions for nitration in nitrobenzene solution and Taylor and Richardson [55] have nitrated with nitrogen dioxide in sulfuric acid solution. Rodd and Everatt [56] have patented the nitration of mixed mononitrotoluenes to produce a dinitrotoluene of certain properties. Cislak, Eastman and Senior [57] have studied the reduction products of 2-nitrofluorene. Wheeler and Cutlar [58] have studied certain aminocymenes with the object of obtaining dyes from them. Several patents on the reduction of nitro compounds under special conditions have been recorded.[59]

A few interesting papers on the sulfur derivatives of the aromatic compounds have appeared. Gebauer-Fülnegg [60] has reported several new aryl sulfur chlorides and sulfur anilides and has made a study of their absorption spectra. Bogert and Smidth [61]

47 Hellerman, *J. Am. Chem. Soc.,* **49**: 1735 (1927).
48 Hellerman and Sanders, *J. Am. Chem. Soc.,* **49**: 1742 (1927).
49 Stephens, *J. Am. Chem. Soc.,* **50**: 186 (1928).
50 Gardner, *J. Am. Chem. Soc.,* **49**: 1831 (1927).
51 Craver, U.S.P. 1636854; 1636855; 1636856 (July 26, 1927); Selden, U.S.P. 1647317 (Nov. 1, 1927); Lewis, U.S.P. 1649833 (Nov. 22, 1927).
52 Pinck, *J. Am. Chem. Soc.,* **49**: 2536 (1927).
53 Wheeler and Brooks, *J. Am. Chem. Soc.,* **49**: 2832 (1927).
54 Livingston and Kyrides, U.S.P. 1638045 (Aug. 9, 1927).
55 Taylor and Richardson, U.S.P. 1640737 (Aug. 30, 1927).
56 Rodd and Everatt, U.S.P. 1657723 (Jan. 31, 1928).
57 Cislak, Eastman and Senior, *J. Am. Chem. Soc.,* **49**: 2318 (1927).
58 Wheeler and Cutlar, *J. Am. Chem. Soc.,* **49**: 2819 (1927).
59 Kahn and Mayer, U.S.P. 1639186 (Aug. 16, 1927); Gubelmann, Weiland and Stallmann, U.S.P. 1654288 (Dec. 27, 1927); Herold and Koppe, U.S.P. 1662421 (March 13, 1928); Davis, U.S.P. 1663476 (March 20, 1928).
60 Gebauer-Fülnegg, *J. Am. Chem. Soc.,* **49**: 2270 (1927).
61 Bogert and Smidth, *J. Am. Chem. Soc.,* **50**: 428 (1928).

have reinvestigated the reaction between sulfur and *p*-toluidine with the view of establishing its mechanism. Hall and Gibbs [62] have obtained some new diazosulfonates by the action of sodium sulfite on diazonium salts under carefully regulated conditions. The diazosulfonates were isolated in syn and anti modifications. Wahl and Lantz [63] have prepared sulfonic acid derivatives of certain hydroxynaphthalenes by the action of sulfurous acid on the cor- responding naphthoquinones. Parmelee [64] has sulfonated β-naph- thol with sulfur trioxide, using nitrobenzene as a solvent. Lynch and Scanlan [65] have continued their study of the pure naphthalene- sulfonic acids and have described the preparation and properties of naphthalene-1,5-disulfonic acid.

Smith and Crawford [66] have investigated the products formed by the action of the Grignard reagent on duroquinone. In general the products are those that would be expected from an α,β-un- saturated ketone. Fieser [67] has made a thorough study of the tautomerism of the hydroxyquinones. He has shown that the equi- librium for any pair of tautomeric hydroxyquinones is a function of their reduction potentials. He has also found [68] that the prop- erties and reactions of 2-hydroxy-1,4-anthraquinone are very similar to those of 2-hydroxy-1,4-naphthoquinone. Wheeler and Carson [69] have studied the bromination of naphthazarin and the structures of the products obtained.

Stouder and Adams [70] have described the synthesis of 1,3-dihy- droxy-4-methylanthraquinone and have shown that it is not identical with rubiadin. This indicated that rubiadin was 1,3-di- hydroxy-2-methylanthraquinone. This structure has since been established by synthesis.[71] The other work of the year in the anthraquinone series has been done in commercial laboratories and is reported in the patent literature. Gubelmann [72] has prepared 2- (or 3-) chloroquinizarin from dichlorophenol, phthalic anhy- dride, sulfuric acid and boric acid. By reduction this has been converted to leucoquinizarin.[73] 1,3-Diamino-2-hydroxy- anthraquinone has been obtained by the action of sulfuric acid on

[62] Hall and Gibbs, *J. Wash. Acad. Sci.*, **17**: 433 (1927).
[63] Wahl and Lantz. U.S.P. 1657809 (Jan. 31, 1928).
[64] Parmelee, U.S.P. 1662396 (March 13, 1928).
[65] Lynch and Scanlan, *Ind. Eng. Chem.* **19**: 1010 (1927).
[66] Smith and Crawford, *J. Am. Chem. Soc.*, **50**: 869 (1928).
[67] Fieser, *J. Am. Chem. Soc.*, **50**: 439 (1928).
[68] Fieser, *J. Am. Chem. Soc.*, **50**: 465 (1928).
[69] Wheeler and Carson, *J. Am. Chem. Soc.*, **49**: 2825 (1927).
[70] Stouder and Adams, *J. Am. Chem. Soc.*, **49**: 2043 (1927).
[71] Mitter and Gupta, *J. Indian Chem. Soc.*, **5**: 25 (1927).
[72] Gubelmann, U.S.P. 1655863 (Jan. 10, 1928).
[73] Gubelmann and Lee, U.S.P. 1655462 (Jan. 10, 1928).

3′,5′-diamino-4-hydroxy-*o*-benzoylbenzoic acid.[74] Thornley [75] has prepared benzoylaminoflavanthrone from flavanthrone and hydroxylamine followed by benzoylation.

Many interesting papers have appeared dealing with the physical properties of organic compounds. Carothers, Bickford and Hurwitz [76] have studied the base strength of a series of amines of the type $C_6H_5(CH_2)_xNH_2$ and have found no indication of alternation. The changes in basicity are continuous but not as regular as would be required by the 1/3 rule of Derick.[77] Williams and Schwingel [78] have reported the dielectric constants and density data for benzene solutions of various aromatic nitro compounds. These data have been applied to the calculation of the electric moments of various solute molecules. Francis [79] has calculated the free energies of certain carbocyclic hydrocarbons. Walton and Finzel [80] have determined the solubility of *m*-nitroaniline in water at temperatures varying from 0° to 83.4°.

Barnes and Fulweiler [81] have determined the absorption bands for benzene and its alkyl derivatives. They have found a progressive shift of the bands toward low frequencies as alkyl groups are added. Orndorff, Gibbs, McNulty and Shapiro [82] have determined absorption curves for benzene and toluene in alcohol solution. Dickinson and Bilicke [83] have obtained new X-ray data on benzene hexachloride and benzene hexabromide which are in agreement with a molecule containing a cyclohexane ring of tetrahedral carbon atoms. De Laszlo [84] has studied the absorption spectra of numerous dichloronaphthalenes. His results indicate that the two halves of the naphthalene molecule are equivalent. Anderson and Gomberg [85] have reported spectroscopic results which show that *p*-hydroxytriphenyl carbinol and *o*-cresyldiphenyl carbinol exist each in two tautomeric modifications, a quinoid and a benzenoid form. Anderson [86] has determined the absorption spectra in the ultraviolet of ether solutions of several triarylmethane derivatives. He has shown that the absorption curve

[74] Gubelmann Weiland and Stallmann, U.S.P. 1659360 (Feb. 14, 1928).
[75] Thornley, U.S.P. 1662872 (March 20, 1928).
[76] Carothers, Bickford and Hurwitz, *J. Am. Chem. Soc.,* **49:** 2908 (1927).
[77] Derick, *J. Am. Chem. Soc.,* **33:** 1167 (1911).
[78] Williams and Schwingel, *J. Am. Chem. Soc.,* **50:** 362 (1928).
[79] Francis, *Ind. Eng. Chem.,* **20:** 277 (1928).
[80] Walton and Finzel, *J. Am. Chem. Soc.,* **50:** 1508 (1928).
[81] Barnes and Fulweiler, *J. Am. Chem. Soc.,* **49:** 2034 (1927).
[82] Orndorff, Gibbs, McNulty and Shapiro, *J. Am. Chem. Soc.,* **50:** 831 (1928).
[83] Dickinson and Bilicke, *J. Am. Chem. Soc.,* **50:** 764 (1928).
[84] De Laszlo, *J. Am. Chem. Soc.,* **50:** 892 (1928).
[85] Anderson and Gomberg, *J. Am. Chem. Soc.,* **50:** 203 (1928).
[86] Anderson, *J. Am. Chem. Soc.,* **50:** 208 (1928).

reported for triphenylchloromethane in alcohol solution is in reality the curve for the ethyl ether of triphenylcarbinol. Orndorff, Gibbs and Shapiro [87] have studied the absorption curves for fluorescein and related compounds. The data show that fluorescein forms salts with hydrochloric and sulfuric acids and that alkalies open the pyrone ring. Porter and Wilbur [88] have studied the ultra violet absorption spectra of acetylchloroaminobenzene and its rearrangement product p-chloroacetanilide. They have found that the radiation of a mercury vapor lamp or heat alone will bring about this rearrangement. The rearrangement will occur in the absence of a solvent and without the appearance of a liquid phase.

Gomberg and Bachmann [89] have studied the reduction of benzil by magnesium subiodide and their results agree with the mechanism which they postulated for the reduction of simple ketones.

Several improved methods for the preparation of known compounds have appeared during the year. Dougherty [90] has given the details for the preparation of benzophenone from o-benzoylbenzoic acid and Marvel and Sperry [91] have described the preparation of the same ketone from benzene, carbon tetrachloride, aluminum chloride and then water. Details for the preparation of benzohydrol,[92] p-bromodiphenyl,[93] m-nitrophenol,[94] di-o-nitrophenyl disulfide,[95] triphenylamine,[96] and benzalaniline [97] have become available. Calcott, Hitch and Mahr [98] have patented a new procedure for the preparation of 2,3-hydroxynaphthoic acid. Marschalk [99] has described a new procedure for the production of perylene and Zinke [100] has described the conversion of perylene to dinitroperylene-3, 10-quinone.

Hann and Jamieson [101] have made the fatty acid amides of 2-methyl-5-isopropylaniline and have suggested that these may be useful derivatives for the identification of the fatty acids.

[87] Orndorff, Gibbs and Shapiro, *J. Am. Chem. Soc.*, **50**: 819 (1928).
[88] Porter and Wilbur, *J. Am. Chem. Soc.*, **49**: 2145 (1927).
[89] Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49**: 2584 (1927).
[90] Dougherty, *J. Am. Chem. Soc.*, **50**: 571 (1928).
[91] Marvel and Sperry, *Organic Syntheses*, **8**: 26 (1928).
[92] Marvel and Hanson, *Organic Syntheses*, **8**: 24 (1928).
[93] Gomberg and Bachmann *Organic Syntheses*, **8**: 42 (1928).
[94] Manske, *Organic Syntheses*, **8**: 80 (1928).
[95] Bogert and Stull, *Organic Syntheses*, **8**: 64 (1928).
[96] Hager, *Organic Syntheses*, **8**: 116 (1928).
[97] Bigelow and Eatnough, *Organic Syntheses*, **8**: 22 (1928).
[98] Calcott, Hitch and Mahr, U.S.P. 1648839 (Nov. 8, 1927).
[99] Marschalk, U.S.P. 1639658 (Aug. 23, 1927).
[100] Zinke, U.S.P. 1642263 (Sept. 13, 1927).
[101] Hann and Jamieson, *J. Am. Chem. Soc.*, **50**: 1442 (1928).

Chapter XXI.

Heterocylic Organic Chemistry.

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While no outstanding developments can be reported as a result of the different investigations carried out in the field of heterocyclic chemistry this past year, the production of new work is very creditable, and the accomplishments will be an encouragement for new workers to till this very fruitful field. The number of heterocyclic groups studied are somewhat limited and are included among the following organic types: dixanthyls, phenanthrenes, quinazolines, thiazoles, piperidines, hydantoins, pyrimidines, isoxazolines, acridines and nucleic acids.

Nucleic Acids. Only one paper dealing with the chemistry of nucleic acids need be mentioned in this report. This is a contribution by Calvery and Remsen,[1] who have contributed new facts increasing our knowledge of the composition of triticonucleic acid. With 100 grams of this rare acid at their command for research they have been able to study more thoroughly its products of degradation. By isolating the same four nucleotides as are formed by hydrolysis of yeast nucleic acid, they have succeeded in securing new and important evidence that these two naturally occurring acids are probably identical.

Hydantoins. The study of polypeptide-hydantoin compounds has been continued by Hahn and her co-workers in Mount Holyoke College. In a joint publication by Hahn and Evans [2] are recorded the results of an incomplete research dealing with the peculiar susceptibility toward light, of certain geometrically unsaturated derivatives containing the polypeptide-hydantoin nucleus. From the results thus far obtained, and reported in this paper,

[1] Calvery and Remsen, *J. Biol. Chem.*, **73**: 593 (1927).
[2] Hahn and Evans, *J. Am. Chem. Soc.*, **49**: 2877 (1927).

on the isomeric modifications of methyl-N-3-methylbenzalhydantoin-N-1-acetate, and of the corresponding cyclic acids,[3] it has been possible to arrive at a more or less detailed knowledge of the conditions favoring these unique isomeric changes. It has now been shown conclusively that the change observed involves either polymerization or an intramolecular rearrangement of a single substance, and that the change is accelerated by light. These characteristic transformations are hastened by bright sunlight and accelerated to a very high degree by exposure to ultraviolet radiation. The exact nature of the isomeric change has not been definitely established.

Hahn and Evans [4] have also contributed an interesting paper dealing with the chemistry of glycyl-N-3-methylphenylalaninehydantoin. The object of the research was to work out a new method of preparing the aminoacid, α-N-methylamino-β-phenylpropionic acid II, previously synthesized by Friedmann and Gutman [5] from α-bromo-β-phenylpropionic acid. This synthesis has now been accomplished by synthesis of the new polypeptidehydantoin represented by formula I, which is found to be easily hydrolyzed by digestion with barium hydroxide giving the required aminoacid II.

$$\begin{array}{c} \text{HOOC.CH}_2\text{N}\!\!-\!\!\!-\!\!\text{CO} \\ | \qquad\quad | \qquad\qquad \xrightarrow{2\text{H}_2\text{O}} \\ \text{CO} \quad\; | \\ | \qquad\quad | \\ \text{CH}_3\text{N}\!\!-\!\!\!-\!\!\text{CHCH}_2\text{C}_6\text{H}_5 \\ \text{I} \end{array}$$

$$\begin{array}{c} \text{NHCH}_3 \\ | \\ \text{C}_6\text{H}_5\text{CH}_2\text{CH.COOH} \;+\; \text{CO}_2 \;+\; \text{NH}_2\text{CH}_2\text{COOH} \\ \text{II} \end{array}$$
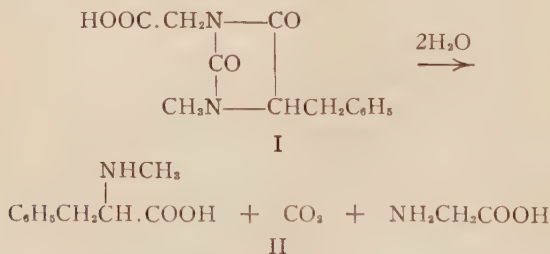
In order to obtain the hydantoin I, the potassium salt represented by formula III was used as the starting point. This underwent alkylation smoothly with formation of the required 3-methyl derivative (IV), which is then reduced to the acid I.

$$\begin{array}{ccc} \text{CH}_3\text{OOC.CH}_2\text{N}\!\!-\!\!\!-\!\!\text{CO} & & \text{KOOC.CH}_2\text{N}\!\!-\!\!\!-\!\!\text{CO} \\ | \qquad\quad | & \xrightarrow{\text{CH}_3\text{I}} & | \qquad\quad | \qquad \longrightarrow \text{I} \\ \text{CO} \quad\; | & & \text{CO} \quad\; | \\ | \qquad\quad | & & | \qquad\quad | \\ \text{KN}\!\!-\!\!\!-\!\!\text{C:CHC}_6\text{H}_5 & & \text{CH}_3\text{N}\!\!-\!\!\!-\!\!\text{C:CHC}_6\text{H}_5 \\ \text{III} & & \text{IV} \end{array}$$
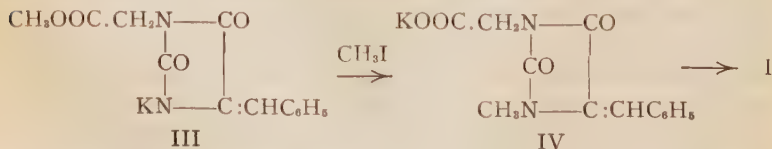
[3] Hahn and Evans, unpublished work.
[4] Hahn and Evans, *J. Am. Chem. Soc.*, **50**: 806 (1928).
[5] Friedmann and Gutman, *Biochem. Z.*, **27**: 491 (1910).

The combinations represented by the ester (V) and the corresponding acid are characterized by the property of occurring in

$$CH_3OOC.CH_2N \underline{\hspace{1cm}} CO$$
$$CO$$
$$CH_3N \underline{\hspace{1cm}} C:CHC_6H_5$$

V
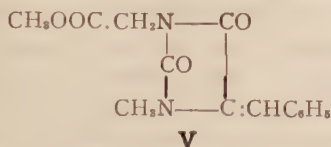
two isomeric or geometrical modifications possessing definite and individual chemical and physical properties. Graphs showing the absorption spectra measurements of the isomeric forms of benzalhydantoin and of its N-3-methyl-N-1-acetic acid derivative are introduced and confirm the speculation that these characteristic pairs of isomers are of the geometrical variety. The absorption spectra measurements enable one to decide with accuracy the question whether substitution in position-3 of the cycle has taken place.

Nicolet and Campbell [6] have succeeded in synthesizing this same amino acid II by an entirely different method. They have shown that the aldehyde condensation products of creatinine offer very convenient constructions as starting points for the synthesis of a-methylamino acids. They have improved on the method developed by Erlenmeyer, Jr.,[7] for the preparation of acetyl-5-benzalcreatinine, obtaining it in a yield of 80% of the theory. Hydrolysis with acids leads smoothly to the formation of 5-benzalcreatinine, while reduction at the double bond, followed by hydrolysis with alkali, gives in excellent yield N-methylphenylalanine (II).

When benzalcreatinine is alkylated with methyl iodide, methylation first takes place on the nitrogen atom in position-2, giving the compound represented by formula VI.

$$NH \underline{\hspace{1cm}} CO$$
$$CH_3N:C$$
$$CH_3N \underline{\hspace{1cm}} C=CHC_6H_5$$

VI
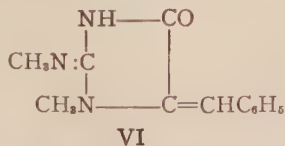
These investigators also found that methylcreatinine prepared according to the method of Korndorfer and Kunze [8] resisted all efforts to bring about a condensation with benzaldehyde. This

[6] Nicolet and Campbell, *J. Am. Chem. Soc.*, **50**: 1155 (1928).
[7] Erlenmeyer, Jr., *Ann.*, **284**: 49 (1895).
[8] Korndorfer, *Arch. Pharm.*, **242**: 641 (1904); Kunze, *ibid.*, **248**: 578 (1910).

failure of methylcreatinine to undergo condensation is not without precedent.[9]

In a paper by Gatewood and Johnson [10] are discussed results obtained in a continuation of research on the behavior of hydrogen sulfide towards nitriles of aminoacids. Their investigation has revealed, however, no outstanding or general reaction. Of the cases thus far examined, three types of reaction have been revealed, namely: (1) formation of dithiopiperazines, as illustrated in the reaction of aminoacetonitrile with hydrogen sulfide; [11] (2) molecular condensation of aminoacetonitriles to imino compounds under the influence of hydrogen sulfide; and (3), the formation of thiodesoxyhydantoins as is illustrated by the interaction of hydrogen sulfide with aminoisobutyronitrile.

Pyrimidines. In the field of pyrimidine chemistry only two papers will be referred to. Dox [12] has shown that 5.5-dialkyl barbituric acids VII interact with Grignard reagents in an unique manner in that two of the carbonyl groups of the pyrimidine cycle are destroyed. In the process, one molecule of water is lost, and the author concludes that a cyclic ether IX (endo ether of 4,6-dihydroxy-4, 5, 5, 6-tetraethyl-2-ketohexahydroxpyrimidine) is the final product of reaction. The change may be expressed as follows:
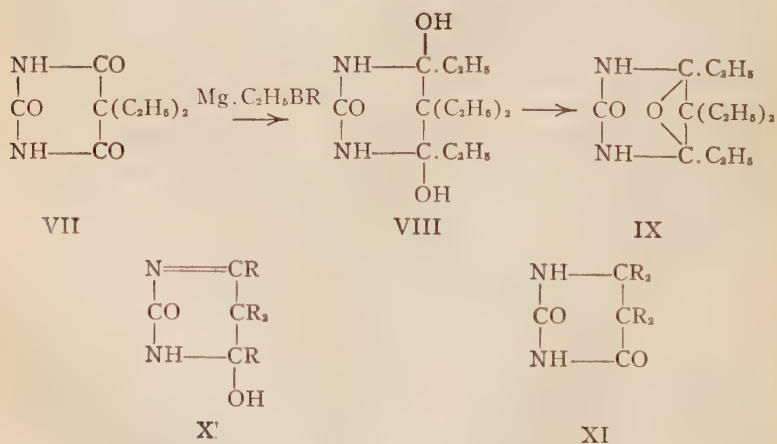
[9] Wheeler and Hoffman, *Am. Chem. J.*, **45**: 368 (1911).
[10] Gatewood and Johnson, *J. Am. Chem. Soc.*, **50**: 1422 (1928).
[11] Johnsen and Burnham, *J. Biol. Chem.*, **9**: 331 (1911).
[12] Dox, *J. Am. Chem. Soc.*, **49**: 2275 (1927).

Other formulas X and XI are proposed for this end product [13] and the correct constitution remains to be determined. In the light of the work of Bauer [14] and Houben [15] formula IX affords at present a satisfactory explanation of structure.

Chi-Ming-Hsueh and Marvel [16] have also contributed to the chemistry of barbituric acids. It is a well known fact that the physiological properties of many optical isomers are different although their physical properties are practically the same in every respect except for action on the plane of polarized light. In order to determine whether optical activity would influence in any way the pharmacological action of hypnotics of the barbituric acid type the authors have investigated the physiological behavior of the racemic and two active modifications of ethyl-*sec.*-octyl-barbituric acid. They find that there is practically no difference in physiological action between the *d*- and *l*-isomers, and the racemic compound. These results tend to confirm the view that physical properties are the most important factor in determining the activity of an hypnotic of this series.

Piperidines. Several contributions have been made in the field of piperidines. McElvain [17] has continued his study of the chemical and pharmacological properties of a number of substituted piperidine-alkyl benzoates including γ-piperidino-propyl benzoate, γ-2-methyl piperidino-propyl benzoate, γ-2-propyl piperidino-propyl benzoate, β-3-methyl piperidino-ethyl benzoate, γ-3-carbethoxy piperidino propyl benzoate, γ-piperidino propyl-*p*-amino benzoate, and γ-3-carbethoxy piperidino propyl-*p*-amino-benzoate. The only compounds of the above series that showed any mucous membrane anesthesia were those in which an alkyl group is substituted in the piperidine nucleus. The compounds containing a carbethoxy constituent in the piperidine nucleus showed no anesthetic action. In general, the substituted piperidino derivatives are less toxic than the corresponding unsubstituted piperidino derivatives.

Thayer and McElvain [18] have continued the senior author's earlier work on 1-alkyl-3-carbethoxy-4-piperidyl *p*-aminobenzoates [19] (XII), which was reviewed in this chapter in 1927. These

[13] Dox, *J. Am. Chem. Soc.*, **49**: 3189 (1927).
[14] Bauer, *Ber.*, **37**: 735 (1904).
[15] Houben, *Ber.*, **37**: 489 (1904).
[16] Chi-Ming Hsueh and Marvel, *J. Am. Chem. Soc.*, **50**: 855 (1928).
[17] McElvain, *J. Am. Chem. Soc.*, **49**: 2835 (1927).
[18] Thayer and McElvain, *J. Am. Chem. Soc.*, **49**: 2862 (1927).
[19] McElvain, *J. Am. Chem. Soc.*, **48**: 2239 (1926).

compounds showed unexpected physiological action and it was found that the size of the alkyl group R in the 1-position had a pronounced effect on physiological activity. New derivatives have been made in which R has been changed to phenyl, benzyl and

$$
\begin{array}{ccc}
CH_2 & \!\!\!-\!\!\! & CH.COOC_2H_5 \\
\mid & & \mid \\
R.N & & CH.O.CO.C_6H_4NH_2 \\
\mid & & \mid \\
CH_2 & \!\!\!-\!\!\! & CH_2
\end{array}
$$
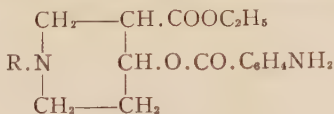
XII

phenylethyl. The pharmacological study on 1-cyclohexyl and 1-phenylethyl-3-carbethoxy-4-piperidyl-p-aminobenzoates shows that the cyclohexyl group does not conform to the higher alkyl groups in its physiological effect, while the introduction of the phenyl-ethyl group leads to a compound over twice as efficient as cocaine. The toxicity of the cyclohexyl compound is slightly greater than that of cocaine, while the toxicity of the phenylethyl compound is one-fifth that of cocaine.

The cyclic aminoalcohol, β-piperidyl carbinol, has been used by Sandborn and Marvel [20] for the synthesis of compounds possessing a local anesthetic action. This alcohol is easily obtained by the reduction of ethyl nicotinate with sodium and ethyl alcohol. Ethyl nipecotate also undergoes reduction to this alcohol by the same reduction method. The derivatives synthesized include a series of nitrogen alkyl compounds which were then converted into the cor-responding esters of p-aminobenzoic acid of the type represented by formula XIII. The methyl, ethyl, isopropyl and n-butyl com-pounds were prepared and it was found that their pharmacological properties compare favorably with those of the local anesthetics now in commercial use.

$$
\begin{array}{ccc}
 & CH_2 & \\
\diagup & & \diagdown \\
CH_2 & & CH.CH_2.O.CO.C_6H_4.NH_2 \\
\mid & & \mid \\
CH_2 & & CH_2 \\
\diagdown & & \diagup \\
 & NR.HCl &
\end{array}
$$
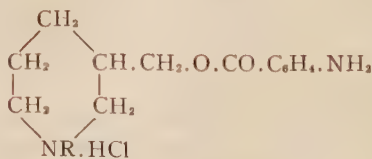
XIII

β-Vinylpiperidine (XIV) is of interest because of its structural relationship to the quinuclidine nucleus of the cinchonine and quinine group of alkaloids. Merchant and Marvel [21] report an

[20] Sandborn and Marvel, *J. Am. Chem. Soc.*, **50**: 563 (1928).
[21] Merchant and Marvel, *J. Am. Chem. Soc.*, **50**: 1197 (1928).

interesting synthesis of this compound from β-piperidyl carbinol, which involves the following intermediate steps:

$$(C_5H_{10}N).CH_2OH \longrightarrow R.CH_2.Br \longrightarrow R.CH_2.CN$$
$$\longrightarrow R.CH_2COOC_2H_5 \longrightarrow R.CH_2.CH_2OH \longrightarrow$$

$$\begin{array}{c} CH_2\text{——}CH_2\text{—}CHCH:CH_2 \\ | \qquad\qquad | \\ CH_2\text{—}CH_2\text{—}NHCH_2 \end{array}$$
$$XIV$$
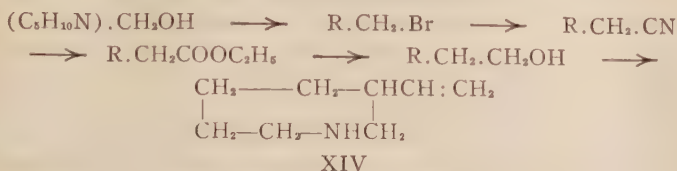
Dehydration of β-piperidyl carbinol with phosphorus pentoxide leads to the formation of β-methylenepiperidine.

Isoxazolines. Several publications in the field of isoxazolines have been contributed by Kohler and his co-workers. The senior author has contributed further to our knowledge of the chemistry of α-bromo-γ-nitro ketones.[22] It is known that certain combinations represented by the type formula XV, are easily converted by interaction with methyl alcohol solutions of potassium acetate into β-hydroxy-γ-oximido esters (XVII).[23]

$$\begin{array}{cc} C_6H_5CH.CHBr.COC_6H_5 \\ | \\ CH_2.NO_2 \end{array} \longrightarrow \begin{array}{c} C_6H_5CH\text{—}CHCOC_6H_5 \\ | \qquad | \\ CH \quad O \\ \diagdown \diagup \\ NO \end{array} \longrightarrow$$

$$\qquad XV \qquad\qquad\qquad XVI$$

$$\begin{array}{c} C_6H_5CH.CHOH.CC_6H_5 \\ | \qquad\qquad \| \\ CH_3OOC \qquad NOH \end{array}$$
$$XVII$$
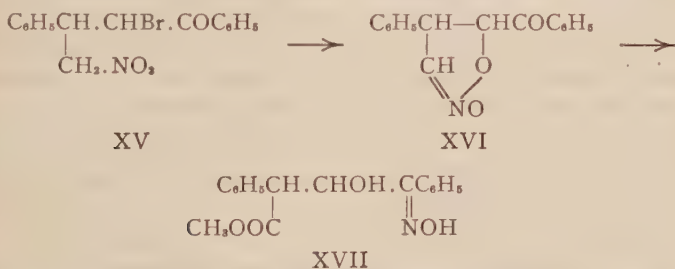
We are not certain regarding the mechanism of this change, but the author concludes from experimental evidence that a primary intermediate or cyclic combination—an isoxazoline oxide (XVI)—is first formed which is then transformed into an hydroxamic ether by action of potassium acetate followed by rearrangement to the oximido ester (XVII).

This work is followed by a paper by Kohler and Blatt[24] in which they describe a method for preparing 3,4-diphenylisoxazolone in quantity. Of the different formulas that may be used to express the constitution of this compound the authors conclude that this substance is to be represented in solution as an equilib-

[22] Kohler, *J. Am. Chem. Soc.*, **50**: 221 (1928).
[23] Kohler and Shohan, *J. Am. Chem. Soc.*, **48**: 2425 (1926); Kohler and Goodwin, *J. Am. Chem. Soc.*, **49**: 219 (1927).
[24] Kohler and Blatt, *J. Am. Chem. Soc.*, **50**: 504 (1928).

rium mixture of *keto* and *enol* forms. While they failed to isolate desmotropic modifications they did, however, secure evidence of the structure of the compound both as a solid and in solution. The possible modifications of diphenylisoxazolone are theoretically expressed by formulas XVIII, XIX, XX.

$$
\begin{array}{cccc}
\underset{\text{XVIII}}{\begin{array}{l} C_6H_5CH\text{—}CO \\ \quad\quad\ |\quad\quad\ >O \\ C_6H_5C\text{==}N \end{array}} &
\underset{\text{XIX}}{\begin{array}{l} C_6H_5C\text{===}COH \\ \quad\quad |\quad\quad >O \\ C_6H_5C\text{==}N \end{array}} &
\underset{\text{XX}}{\begin{array}{l} C_6H_5C\text{——}CO \\ \quad\quad ||\quad\quad >O \\ C_6H_5C\text{——}NH \end{array}} &
\underset{\text{XXI}}{\begin{array}{l} C_6H_5C\text{——}CO \\ \quad\quad ||\quad\quad >O \\ C_6H_5C\text{——}N.CH_3 \end{array}}
\end{array}
$$
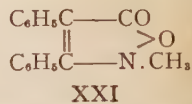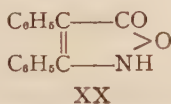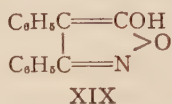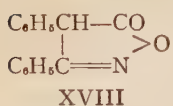
Reactivity with bromine according to Kurt Meyer's method, and behavior of the isoxazoline and its alkyl and acyl derivatives towards ozone and Grignard reagents all argue in favor of two forms of the isoxazolone in solution corresponding to XVIII and XIX. Alkylation with methyl iodide was accomplished in many ways, all of which lead to the same methyl derivative XXI. In their last paper Kohler and Blatt [25] discuss new facts revealed by their further study of the methyl compound represented by formula XX. Interaction of this cycle with a Grignard reagent $(C_6H_5Mg\cdot Br)$ leads to the formation of salts of the corresponding hydroxy isoxazolines. These may be viewed as either ammonium or oxonium salts XXII and XXIII. The hydroxides or bases corresponding to these two salts would be expected to revert to the

$$
\underset{\text{XXII}}{\left[\begin{array}{l} C_6H_5C\text{==}C.C_6H_5 \\ \quad |\quad\quad\ >O \\ C_6H_5C\text{==}N.CH_3 \end{array} \right] X}
\qquad\qquad
\underset{\text{XXIII}}{\left[\begin{array}{l} C_6H_5C\text{—}C.C_6H_5 \\ \quad ||\quad\quad >O \\ C_6H_5C\text{—}N.CH_3 \end{array} \right] X}
$$
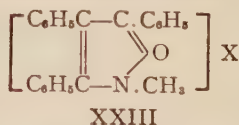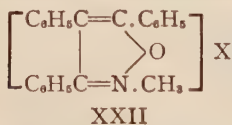
same pseudo base. The authors have been able to contribute important data bearing on these tautomeric changes by making a thorough study of the properties of the salt of the cyclic compound (methyl triphenyl-hydroxyisoxazoline) represented by formula

$$
\underset{\text{XXIV}}{\begin{array}{l} C_6H_5C\text{==}C.C_6H_5 \\ \quad |\quad\quad\ >O \\ C_6H_5C\text{—}N.CH_3 \\ \quad\ | \\ \quad OH \end{array}}
\qquad\qquad
\underset{\text{XXV}}{\begin{array}{l} C_6H_5CH.COC_6H_5 \\ \quad\ | \\ C_6H_5C\text{—}N(OH)CH_3 \\ \quad\ | \\ \quad OH \end{array}}
$$
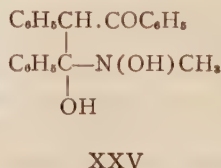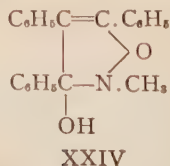
XXIV. They find that this substance undergoes all the changes characteristic of pseudo bases. The halide salts of the base are characterized by their property of forming unique complex double

[25] Kohler and Blatt, *J. Am. Chem. Soc.*, **50**: 1217 (1928).

salts with ferric chloride. Decomposition of the latter with alkali leads to the formation of the pseudo base which is an oil. Whether this corresponds in structure to formula XXIV or XXV could not be established.

Indoles. The synthesis of 2-oxohexahydro-benzfuran-3-propionic acid (XXVI) was accomplished by Kendall and Osterberg [26] in 1926. These workers have now extended their investigation of the characteristic reactions of this interesting substance and conclusive proof of its structure is furnished.[27] They have also incorporated into their researches an intensive study of the chemical properties of 2-oxohexahydroindole-3-propionic acid [28] (XXVII) and have produced new evidence supporting the constitution previously assigned to it. The research reported is confined chiefly to the study of halogenated derivatives and the determination of their correct constitution.
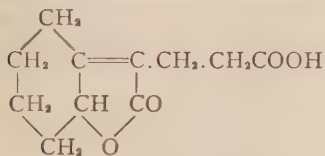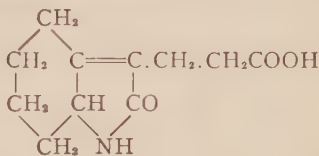
CH₂   CH₂
CH₂ C═══C.CH₂.CH₂COOH   CH₂ C═══C.CH₂.CH₂COOH
CH₂ CH CO   CH₂ CH CO
CH₂ O   CH₂ NH
XXVI   XXVII

Dixanthyls. Conant and Garvey [29] have contributed further to our knowledge of free radicals by continuing the work started in the Harvard laboratory on the chemistry of alkylated dixanthyls.[30] New data dealing with the reactions of organic constructions functioning as free radicals have been obtained by investigation of the properties of dixanthyl and its corresponding dixanthyl-9,9'-dicarboxylic acid.

They find that both compounds undergo characteristic cleavage reactions when subjected to the action of bromine, sodium-potassium alloy, sodium amalgam, concentrated sulfuric acid, and by oxidation above 150°. In fact, both compounds act like dissociable ethanes, and in their chemical behavior illustrate a remarkable parallel between the reactions of single carbon bonds and addition reactions of ethylene compounds.

[26] Kendall and Osterberg, *J. Am. Chem. Soc.*, **48**: 1384 (1926).
[27] Kendall and Osterberg, *J. Am. Chem. Soc.*, **49**: 2047 (1927).
[28] Osterberg and Kendall, *J. Am. Chem. Soc.*, **42**: 2616 (1920); Brunel, *Ann. chim. phys.* **61**: 253 (1905).
[29] Conant and Garvey, *J. Am. Chem. Soc.*, **49**: 2080, 2599 (1927).
[30] Conant and Sloan, *J. Am. Chem. Soc.*, **47**: 572 (1925); Conant and Small, *J. Am. Chem. Soc.*, **47**: 3068 (1925); Conant, Small and Sloan, *J. Am. Chem. Soc.*, **48**: 1743 (1926).

Phenanthrenes. Moore and Huntress [31] contribute the only paper in the field of phenanthrene chemistry. They show that 2-nitrofluorenone and hydroxylamine interact to form an oxime, which easily undergoes a Beckmann rearrangement under the influence of phosphorus pentachloride or phosphorus oxychloride. The transformation is quantitative with formation of 7-nitro-phenanthridone. The process serves admirably as a method of preparation of this cyclic amide.

Selective Reduction. Bray and Adams [32] have extended further the practical application of their catalytic reduction method by using hydrogen and platinum-oxide platinum black in the presence of certain promoters.[33] They show that furfuracrolein (XXVIII) is reduced smoothly by their catalytic method in presence of a promoter (ferrous sulfate and zinc acetate) giving the corresponding unsaturated alcohol represented by formula XXIX. By using ferrous sulfate alone as the promoter the reaction does not stop automatically at the alcohol but more hydrogen

$$
\begin{array}{ccc}
\text{CH—CH} & & \text{CH—CH} \\
\| \quad \| & & \| \quad \| \\
\text{CH} \quad \text{C.CH:CH.CHO} & \longrightarrow & \text{CH} \quad \text{C.CH:CH.CH}_2\text{OH} \\
\diagdown \diagup & & \diagdown \diagup \\
\text{O} & & \text{O} \\
\text{XXVIII} & & \text{XXIX}
\end{array}
$$
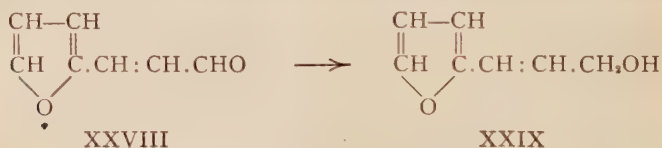
is absorbed with production of higher reduced products which are difficult to separate in a pure state and in good yield.

Thiazoles. An improvement over Sebrell and Boord's [34] method of preparing 2-mercaptobenthiazoles is accomplished by Teppema and Sebrell [35] by starting with o-nitrochlorbenzene, a comparatively cheap material. The three usual stages of reaction leading to the thiazole constructions from an o-compound of this type are expressed as follows:

$$Cl.C_6H_4NO_2 + Na_2S_2 = NO_2C_6H_3.S.S.C_6H_4NO_2 + 2NaCl$$

$$NO_2C_6H_4.S.SC_6H_4.NO_2 + 14NaSH = 2NH_2C_6H_4SH + 4H_2O + 7Na_2S + 7S$$

$$NH_2C_6H_4SH + CS_2 = C_6H_4 \underset{S}{\overset{N}{<}} C.SH + H_2S.$$
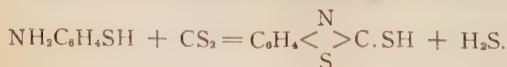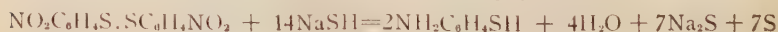
[31] Moore and Huntress, *J. Am. Chem. Soc.*, **49**: 2618 (1927).
[32] Bray and Adams, *J. Am. Chem. Soc.*, **49**: 2101 (1927).
[33] Carothers and Adams, *J. Am. Chem. Soc.*, **45**: 1071 (1923); **46**: 1675 (1924); Tuley and Adams, *J. Am. Chem. Soc.*, **47**: 3061 (1925); Adams and Garvey, *J. Am. Chem. Soc.*, **48**: 477 (1926); Kaufmann and Adams, *J. Am. Chem. Soc.*, **45**: 3029 (1923).
[34] Sebrell and Boord, *J. Am. Chem. Soc.*, **45**: 2390 (1923).
[35] Teppema and Sebrell, *J. Am. Chem. Soc.*, **49**: 1748 (1927).

The authors accomplish all these reactions in one step by heating the *o*-nitrochlorbenzene directly with sodium hydrosulfide (prepared by saturation of sodium sulfide with hydrogen sulfide) and carbon bisulfide, thereby obtaining easily an 87% yield of the required 2-mercaptobenzthiazole. Substituted 1-chloro-2-nitrobenzene compounds can be used in the reaction, but the synthesis fails, however, for the preparation of dihalogenated 2-mercaptothiazoles. On account of the practical utility of several of these combinations as accelerators in the rubber industry the authors [36] have incorporated into their researches the study of nitration of the mercaptobenzthiazoles and their corresponding reduction products or amines from which new derivatives of importance have been synthesized by application of Sandmeyer's reaction.

Quinazolines. In this field of cyclic combinations containing sulfur Bogert and McColm [37] report on a pharmacodynamic study of certain quinazoline compounds carried out in coöperation with A. D. Hirschfelder of the University of Minnesota and E. W. Rockwood of the University of Iowa. The work was undertaken in an attempt to throw additional light upon the relationship between chemical constitution and physiological action.

Quinazolines of the atophan type were studied, being really an extension of the earlier work of Bogert and Nabenhauer.[38] The plan of synthesis developed by the latter was followed and consisted in the preparation of the substituted *o*-aminoacetophenone, its oxidation to the corresponding isatinic acid and conversion of the latter into the required quinazoline derivative by heating it with alcoholic ammonia under pressure. Various quinazoline derivatives of the cincophene type have been obtained by application of these reactions and their pharmacological action is now being investigated.

Organic compounds containing selenium—benzoselenazols— have also been synthesized by methods entirely analogous to those developed in the Columbia laboratories for the preparation of the corresponding benzthiazoles. The arsenic combination 2-phenylbenzoselenazole-4-arsonic acid was prepared but it was found to have no curative action when tested upon mouse tumors.

[36] Teppema and Sebrell, *J. Am. Chem. Soc.*, **49**: 1779 (1927).
[37] Bogert and McColm, *J. Am. Chem. Soc.*, **49**: 2650 (1927).
[38] Bogert and Nabenhauer, *J. Am. Chem. Soc.*, **46**: 1702 (1924).

Chapter XXII.

Metallo-Organic Compounds.

Henry Gilman,

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By an organometallic compound we mean a compound having carbon attached directly to a metal. In this sense, the iron carbide in steels is an organometallic compound. We are less familiar with the term "metallo-organic," but because it includes organic compounds of arsenic, antimony, etc., we take it that the expression refers to those compounds having carbon attached not only to metals but also to metalloids. No mention is made here of the several pharmacological studies on arsenicals, antimonials, etc. These are treated elsewhere in the Survey.

Elements of Group I. *Lithium.* Marvel, Hager and Coffman[1] in a study of the reaction between lithium *n*-butyl and various organic halogen compounds observed that, in general, the simple reaction of replacement of halogen by the *n*-butyl group does not occur. The products obtained suggest the intermediate formation of free radicals. Unusual results were obtained with the three bromotoluenes, the *o*- and *m*- giving toluene almost quantitatively and the *p*- a high yield of *p*-*n*-butyltoluene.

Sodium and Potassium. Conant and Garvey,[2] in continuation of their extensive studies on free radicals, have shown that it is possible to differentiate between certain compounds which contain a reactive carbon to carbon linkage by using the liquid sodium-potassium alloy and the 40% and 1% sodium amalgams. The cleavage reactions of dixanthyl (which are slower than with hexaphenylethane) quite probably do not proceed through a free radical and are concerned with definite reactions of the single bond. The organosodium or organopotassium products were identified and estimated, after treatment with carbon dioxide, as

[1] Marvel, Hager and Coffman, *J. Am. Chem. Soc.*, **49**: 2323 (1927).
[2] Conant and Garvey, *J. Am. Chem. Soc.*, **49**: 2080, 2599 (1927).

the carboxylic acids. The same reactions were used by Salzberg and Marvel [3] in a study of their very interesting hexa-*tert.*-butyl-ethynylethane. Cleavage reactions with alkali metals indicate that the stability of the central ethane linkage is intermediate between that of the corresponding linkages in dibenzyl and hexaphenyl-ethane.

The several petroleum investigations recently initiated have already begun to yield promising results. Conant and Blatt [4] treated various crude petroleums and cracking oil residues with sodium-potassium alloy ; the organometallic derivatives so obtained were probably formed by addition of the metal to an unsaturated system, inasmuch as they showed that the alloy adds to propyl-styrene and dimethylstyrene. These results have an importance beyond the characterization of petroleum and the dissociation and disproportionation studies of substituted ethanes, for recent work [5] on the mechanism of polymerization of unsaturated hydrocarbons by alkali metals points to the intermediate formation of complex organo-alkali compounds. Obviously, such polymerization is of importance in studies on synthetic rubber.

The work of Bachmann and Clarke [6] on the mechanism of the Würtz-Fittig reaction, wherein it is shown that the reaction may be conveniently interpreted by assuming the intermediate forma-tion of free radicals, emphasizes some of the special contributions to organic chemistry by manufacturers and dealers in research chemicals. There are very few laboratories that can afford a study of reactions for which unusual quantities of expensive materials are necessary in order to isolate small but important fractions.

Jones and Seymour,[7] in a study of the reaction between sodium triphenylmethyl and trimethylmethoxyammonium iodide, noted that trimethylmethoxyammonium triphenylmethyl (the probable primary reaction product) decomposed to give trimethylamine, triphenylmethane, diphenylethanol and sodium iodide.

In studies in liquid ammonia solution, Wooster [8] prepared both mono- and disodium derivatives of benzophenone, and from a study of their reactions proposed that addition reactions is a more general property of metal ketyls than has been hitherto supposed.

[3] Salzberg and Marvel, *J. Am. Chem. Soc.*, **50**: 1737 (1928).
[4] Conant and Blatt, *J. Am. Chem. Soc.*, **50**: 542, 551 (1928); cf. reference 54.
[5] Ziegler and Bahr, *Ber.*, **61**: 253 (1928); *see also* Willstätter, Seitz and Bumm, *Ber.*, **61**: 871 (1928).
[6] Bachmann and Clarke, *J. Am. Chem. Soc.*, **49**: 2089 (1927).
[7] Jones and Seymour, *J. Am. Chem. Soc.*, **50**: 1150 (1928).
[8] Wooster, *J. Am. Chem. Soc.*, **50**: 1388 (1928).

Rising and Zee's [9] study of the behavior of the sodium salts of phenylacetonitrile and α-phenylbutyronitrile suggests for them carbide structures in a tautomeric relationship with the nitride form.

Copper and Silver. Hill and Tyson [10] have found alcoholic silver nitrate more suitable than ammoniacal cuprous chloride for the determination of 1-heptine.

Elements of Group II. *Beryllium.* Gilman and Schulze [11] have prepared and investigated the properties of a number of beryllium dialkyls and diaryls. They are more reactive, in general, than the Grignard reagents. The organoberyllium halides prepared by the same authors [12] are less active than the corresponding Grignard reagents. The following probable equilibrium, $BeR_2 + BeX_2 \rightleftarrows 2RBeX$, is of interest in connection with a number of recent studies on the constitution of the Grignard reagent. It has been proposed [13] that the organomagnesium halides are better represented as $MgR_2 . MgX_2$ and not as $RMgX$.

Magnesium. Gilman and Schulze [14] have shown that magnesium diethyl is a solid and that, contrary to early work by others, it reacts in an expected manner with acetyl chloride.

One of the most outstanding contributions to organometallic chemistry in recent years, the reactions of magnesious halides with organic compounds, has stimulated new work both in this country and abroad. The discoverers of this new abnormally valented complex, Gomberg and Bachmann,[15] have extended the studies of their binary systems ($Mg—MgI_2$ and $Mg—MgBr_2$ as well as $Be—BeI_2$ and $Zn—ZnI_2$) to benzil. This diketone was quantitatively reduced by their binary systems to the halomagnesium salt of stilbenediol, $C_6H_5C(OMgX)=(XMgO)CC_6H_5$. These unsaturated glycolates were found to be extremely reactive with various reagents and it is possible that there is a partial opening of the double bond to a single bond, giving rise to two reactive trivalent carbon atoms in the same molecule. Fieser [16] has used the magnesium subiodide in a 1,6-addition to *p*-quinones and a 1,4-addition

[9] Rising and Zee, *J. Am. Chem. Soc.,* **50:** 1699 (1928).
[10] Hill and Tyson. *J. Am. Chem. Soc.,* **50:** 172 (1928); *see also* Guest, *J. Am. Chem. Soc.,* **50:** 1744 (1928).
[11] Gilman and Schulze, *J. Chem. Soc.,* **1927:** 2663
[12] Gilman and Schulze, *J. Am Chem. Soc.,* **49:** 2904 (1927).
[13] Meisenheimer and Schlichenmaier, *Ber.,* **61:** 720 (1928). References to earlier work are contained in this article which in itself shows that the Grignard reagent is monomolecular in dilute solutions and, therefore, best represented as $RMgX$.
[14] Gilman and Schulze, *J. Am. Chem. Soc.,* **49:** 2328 (1927).
[15] Gomberg and Bachmann, *J. Am. Chem. Soc.,* **49:** 2584 (1927).
[16] Fieser, *J. Am. Chem. Soc.,* **50:** 439 (1928).

to *o*-quinones. Gauerke and Marvel [39] did not succeed in reducing dicyclohexyl ketone by means of magnesious iodide.

The Grignard Reagent. Hufferd [17] has recommended anhydrous aluminum bromide as a starter for the preparation of some Grignard reagents. Gilman, Peterson and Schulze,[18] in a comparative study of various catalysts, have found that an activated Mg-Cu alloy containing 12.75% copper is more effective than Baeyer's activated magnesium. The yields of some Grignard reagents in solvents other than ethyl ether, in ether-hydrocarbon mixtures and in varying concentrations of ether have been determined by Gilman and McCracken.[19] Some optimal conditions for the preparation of *tert.*-butylmagnesium chloride have been determined by Gilman and Zoellner,[20] and with these conditions as a basis directions have been worked out by Puntambeker and Zoellner [21] for the preparation of trimethylacetic acid in distinctly improved yields. Smith, Boord, Adams and Pease [22] have directed attention to the traces of benzene that may be present in some commercial ethers and so carried over to compounds prepared by means of the Grignard reaction. The sensitive color test of Gilman and Schulze [23] for Grignard reagents and other reactive organometallic compounds is given by *tert.*-butyl- and *tert.*-amylmagnesium halides even in low concentrations, if a few minutes are allowed to elapse before hydrolysis and the addition of the acetic acid-iodine solution. *α*-Naphthyl isocyanate has been recommended by Gilman and Furry [24] for the identification of reactive organometallic compounds. The *α*-naphthalides formed in this manner may also be used for the identification, by indirect means, of the halides used in the preparation of the organometallic compounds. In this connection, Hill [25] has extended earlier work on the identification of alkyl and aryl halides by treating the RMgX compounds formed from such halides with mercuric bromide to form RHgBr compounds that are readily characterized by a melting point determination. Hill's extension includes secondary alkyl and aryl bromides and iodides.

Kohler, Stone and Fuson [26] have described an apparatus for

[17] Hufferd, *J. Am. Chem. Soc.*, **49**: 1845 (1927).
[18] Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**: 19 (1928).
[19] Gilman and McCracken, *Rec. trav. chim.*, **46**: 463 (1927).
[20] Gilman and Zoellner, *J. Am. Chem. Soc.*, **50**: 425 (1928).
[21] Puntambeker and Zoellner, *Organic Syntheses*, **8**: 104 (1928).
[22] Smith, Boord, Adams and Pease, *J. Am. Chem. Soc.*, **49**: 3137 (1927).
[23] Gilman and Schulze, *Bull. soc. chim.*, **41**: 1479 (1927).
[24] Gilman and Furry, *J. Am. Chem. Soc.*, **50**: 1214 (1928).
[25] Hill, *J. Am. Chem. Soc.*, **50**: 167 (1928).
[26] Kohler, Stone and Fuson, *J. Am. Chem. Soc.*, **49**: 3181 (1927).

determining simultaneously the amount of gas evolved and the amount of reagent consumed in reactions between methylmagnesium iodide and organic compounds. The apparatus which is ingenious, workable and accurate should be of great value in oxidation and reduction Grignard reactions that are accompanied by the evolution of gas not due to the presence of active hydrogen. Gilman and Fothergill [27] have shown that the Zerewitinoff method for the estimation of active hydrogen is unreliable with molecules containing a nitro, nitroso or azo group, and that for this reason the cyclic hydroxy structure proposed for o-nitrobenzaldehyde has no support on the basis of gas evolved.

Dufford, Nightingale and Gaddum [28] have studied the luminescence of Grignard reagents in electrical and magnetic fields. Dufford [29] has shown that the reason for the previous discordant observations on chemiluminescence of Grignard reagents by oxidation in ether probably lies in the effect of concentration, so that it is unnecessary for magnesium to be attached directly to an unsaturated carbon atom. The brightness of light is not proportional to the molecular weight of the organomagnesium halide.

New evidence has been presented by Gilman and Harris [30] and Gilman and McGlumphy [31] on the non-addition of the Grignard reagent to an ethylenic linkage. In one [30] of these studies it was shown that cinnamylmagnesium chloride, like benzyl- and triphenylmethylmagnesium chlorides,[32] undergoes rearrangement in some reactions. In reactions with alkylbarbituric acids, Dox's [33] work indicates that a carbonyl group is alkylated by two molecules of an RMgX compound with the loss of a molecule of water. Blicke [34] has shown that under certain conditions triphenylmethyl (isolated as the peroxide) is formed in the interaction of carbon dioxide and phenylmagnesium bromide. As yet, there is no satisfactory explanation for the formation of the free radical. In the same study, reactions were carried out with a-naphthylmagnesium bromide and carbon dioxide, acid chlorides, nitriles and ethyl formate.

27 Gilman and Fothergill, J. Am. Chem. Soc., 49: 2815 (1927); 50: 867 (1928).
28 Dufford, Nightingale and Gaddum, J. Am. Chem. Soc., 49: 1858 (1927).
29 Dufford, J. Am. Chem. Soc., 50: 1822 (1928).
30 Gilman and Harris, J. Am. Chem. Soc., 49: 1825 (1927).
31 Gilman and McGlumphy, Rec. trav. chim., 47: 418 (1928).
32 The preparation of triphenylacetaldehyde by Hellerman, Cohn and Hoen (J. Am. Chem. Soc., 50: 1716 (1928)) shows that Schmidlin did not prepare this aldehyde from triphenylmethylmagnesium chloride and ethyl formate.
33 Dox, J. Am. Chem. Soc., 49: 2275, 3189 (1927).
34 Blicke, J. Am. Chem. Soc., 49: 2843 (1927).

Bateman and Marvel [35] have carried out some standard Grignard reactions with new compounds in correcting earlier work by Schlenck on the structure of the hydrocarbon obtained by the dehydration of *tert*.-butyldiphenyl carbinol. The hydrocarbon was identified as 3,3-diphenyl-2-methyl-1-butene. The extensive studies of Kohler on tautomerism in the isoxazole series has been continued with Blatt.[36] They found that diphenyl-isoxazolone consumed but one molecule of methylmagnesium iodide, and that the halogen-magnesium derivatives reacted with standard reagents for the characterization of the -MgX group to give products that limited the number of possible ketonic and enolic modifications. The proof of structure of these unsaturated heterocyclic compounds containing both oxygen and nitrogen in the ring presents extra experimental difficulties because of the several possible types of tautomerism. Phenylmagnesium bromide with 2-methyl-3,4-diphenylisoxazolone gave on hydrolysis with 40% hydrobromic acid α,β-diphenylbenzalacetophenone and a cyclic ammonium bromide.

Arylsulfonylmagnesium chlorides have been prepared by Gilman and Fothergill [37] by the direct reaction in ether solution between arylsulfonyl chlorides and magnesium. The reaction between quinones and the Grignard reagent is depressingly complex. Smith and Crawford [38] wisely selected duroquinone (tetramethylbenzoquinone) and phenylmagnesium bromide for an extensive study of this reaction. Despite their choice of a quinone and an RMgX compound that would give the smallest number of side reactions, they found that about 80% of the reaction product was an oil that could neither be crystallized nor distilled without decomposition. The oil may be a mixture of stereoisomers. Insofar as a quinone is comparable with an α,β-unsaturated ketone, the solid products actually isolated and identified are those which would be expected. Gauerke and Marvel,[39] in a study of the action of cyclohexylmagnesium bromide on derivatives of oxalic acid, found that this Grignard reagent showed essential differences from phenylmagnesium bromide. Coleman and Hauser [40] have extended the synthetic value of RMgX compounds to include the preparation of primary amines from monochloroamine. In this reaction

[35] Bateman and Marvel, *J. Am. Chem. Soc.*, **49**: 2914 (1927).
[36] Kohler and Blatt, *J. Am. Chem. Soc.*, **50**: 504, 1217 (1928).
[37] Gilman and Fothergill, *J. Am. Chem. Soc.*, **50**: 802 (1928).
[38] Smith and Crawford, *J. Am. Chem. Soc.*, **50**: 869 (1928).
[39] Gauerke and Marvel, *J. Am. Chem. Soc.*, **50**: 1178 (1928).
[40] Coleman and Hauser, *J. Am. Chem. Soc.*, **50**: 1193 (1928).

the yield of amine decreases with the increasing atomic weight of halogen in the organomagnesium halide. Rossander and Marvel [41] have described conditions for the introduction of the γ-chloropropyl group in satisfactory yields. In their studies with γ-chloropropyl p-toluenesulfonate they also obtained RX compounds, the halogen in this case coming from the RMgX compound. This constitutes an extension of the utility of the alkyl or halogenoalkyl sulfonate reaction.

In a study of the reaction with several isocyanides and hydrogen cyanide, Gilman and Heckert [42] obtained benzaldehyde (in very poor yields) only from methyl isocyanide with phenylmagnesium bromide. The formation of benzaldehyde is not unequivocal proof of the bivalence of carbon in methyl isocyanide.

Adams and collaborators in their comprehensive and excellent studies on physiological action and chemical constitution prepared cyclopentanecarboxylic acid from cyclopentylmagnesium bromide; [43] various primary alcohols from formaldehyde and from ethylene oxide; [44] hydroxy esters from aldehydo-esters and keto esters from acid chloride-esters; [45] and, cyclopentenyl-ethyl alcohols and esters from related reactions with the Grignard reagent prepared from cyclopentenyl-ethyl bromide.[46] Allen and Rosener [47] could not prepare the Grignard reagent from 2,3,5-triphenyl-4-bromofuran. This is hardly unexpected because of the extreme inertness of the bromine even towards hot alcoholic potash.

Norris and Cortese [48] used standard procedures for the preparation of a number of the alcohols employed in their reactivity studies. Carothers, Bickford and Hurwitz [49] do not recommend the ethylene oxide synthesis for the preparation of alcohols of the $C_6H_5(CH_2)_4$-series. Reed, Lathrop and Chandler [50] synthesized several chlorohydrins from epichlorohydrin. Olson and Meyers [51] prepared ethane, used in their hydrogen-ethylene reaction in the presence of excited mercury atoms, from ethylmagnesium iodide. Stephens [52] synthesized a number of α-phenyl carbinols from

[41] Rossander and Marvel, *J. Am. Chem. Soc.*, **50**: 1491 (1928).
[42] Gilman and Heckert, *Bull. soc. chim.*, **43**: 224 (1928).
[43] Talbot and Adams, *J. Am. Chem. Soc.*, **49**: 2040 (1927).
[44] Adams, Stanley, Ford and Peterson, *J. Am. Chem. Soc.*, **49**: 2934 (1927); Yohe and Adams, *J. Am. Chem. Soc.*, **50**: 1503 (1928).
[45] Davies and Adams, *J. Am. Chem. Soc.*, **50**: 1749 (1928).
[46] Arvin and Adams, *J. Am. Chem. Soc.*, **50**: 1790 (1928).
[47] Allen and Rosener, *J. Am. Chem. Soc.*, **49**: 2110 (1927).
[48] Norris and Cortese, *J. Am. Chem. Soc.*, **49**: 2640 (1927); *see also* Norris and Blake, *J. Am. Chem. Soc.*, **50**: 1808 (1928).
[49] Carothers, Bickford and Hurwitz, *J. Am. Chem. Soc.*, **49**: 2908 (1927).
[50] Reed, Lathrop and Chandler, *J. Am. Chem. Soc.*, **49**: 3116 (1927).
[51] Olson and Meyers, *J. Am. Chem. Soc.*, **49**: 3131 (1927).
[52] Stephens, *J. Am. Chem. Soc.*, **50**: 186 (1928).

aldehydes and ketones. Improved directions for the preparation of selenophenol from selenium and phenylmagnesium bromide have been described by Foster and Brown.[53] Lucas and Dillon [54] prepared butene-1 from allyl bromide and methylmagnesium bromide. The same authors [55] obtained pentan-2-ol and nonan-5-ol (but no heptan-3-ol) by the successive addition of ethylmagnesium bromide and *n*-butyl-magnesium bromide to ethyl formate. The heptan-3-ol was prepared from propionaldehyde and *n*-butyl-magnesium bromide.

Other syntheses involving the Grignard reagent are to be found in References 3, 4, 6, 11, 59 and 60.

Barium. Gilman and Schulze [56] prepared ethylbarium iodide and phenylbarium iodide. These organobarium iodides, like the corresponding organocalcium iodides, are prepared with greater difficulty and are less active than the Grignard reagents.

Mercury. Harden [57] prepared monohydroxymercurisalicyl-sulfonphthalein from salicylsulfonphthalein and mercury acetate. Other syntheses involving mercury are to be found in References 11, 25 and 59.

Elements of Group III. *Aluminum.* Prescott and Hincke [58] have made equilibrium studies of carbon monoxide and aluminum carbide prepared from aluminum oxide and carbon.

Elements of Group IV. *Germanium.* Orndorff, Tabern and Dennis [59] have continued their extensive studies of organo-germanium compounds, especially those containing potential solubilizing groups with a view to their possible pharmacological application. Many of their new compounds were prepared from germanium tetrachloride or organogermanium halides with Grignard reagents or from mercury dialkyls and diaryls.

Lead. Gilman and Robinson [60] have reported improved directions for the preparation of tetraphenyllead from lead chloride and phenylmagnesium bromide. The same authors [61] have worked out a convenient method of analysis for total lead in essentially non-volatile organolead compounds.

[53] Foster and Brown, *J. Am. Chem. Soc.,* **50**: 1182 (1928).
[54] Lucas and Dillon, *J. Am. Chem. Soc.,* **50**: 1460 (1928).
[55] Lucas and Dillon, *J. Am. Chem. Soc.,* **50**: 1711 (1928).
[56] Gilman and Schulze. *Bull. soc. chim.,* **41**: 1333 (1927).
[57] Harden, *J. Am. Chem. Soc.,* **49**: 3139 (1927).
[58] Prescott and Hincke, *J. Am. Chem. Soc.,* **49**: 2753 (1927)
[59] Orndorff, Tabern and Dennis, *J. Am. Chem. Soc.,* **49**: 2512 (1927).
[60] Gilman and Robinson, *J. Am. Chem. Soc.,* **49**: 2315 (1927).
[61] Gilman and Robinson, *J. Am. Chem. Soc.,* **50**: 1714 (1928).

Thorium. Thorium carbide has been studied by Prescott and Hincke [62] in connection with the high-temperature equilibrium between thorium oxide and carbon.

Elements of Group V. *Arsenic.* Hamilton and Jelinek [63] prepared 3,4-dicarboxyphenylarsonic acid by the Bart method of arsonation from dimethyl-4-aminophthalate. The anhydride, esters and salts of this arsonic acid were also prepared and their properties studied.

Jurist and Christiansen [64] have shown that the arsenite method of analysis gives a more accurate distribution of the sulfur in neoarsphenamine than has previously been possible. They found that the so-called "sulfarsphenamine sulfur" is, in fact, nuclear sulfur; that there are probably two types of combination between arsphenamine base and sodium formaldehyde sulfoxylate, one being of the N-methylene type, and the other resembling a double salt formation; and, that there is a type of sulfur present in neoarsphenamine which owes its origin to some reaction or decomposition of sodium formaldehyde sulfoxylate.

Palmer and Scott [65] have found that arsenobenzene has a molecular weight corresponding to the monomolecular azo type structure in a non-associating solvent, but that it is distinctly associated in benzene and in naphthalene solutions; and that, in view of these determinations and the penta-molecular form of arsenomethane, the custom of representing all arseno compounds by the general formula $R-As=As-R$ is unjustified.

Edee,[66] in connection with the preparation of soluble aliphatic-aromatic arseno compounds, developed improved directions for the preparation of β-hydroxyethylarsonic acid and then, by the simultaneous reduction of this aliphatic with various aromatic arsonic acids, prepared a series of aryl arsenoethanols. Also, a previously unknown unsymmetrical aliphatic-aromatic triarseno type was prepared.

Jacobs and Heidelberger [67] have described improved directions for the preparation of *p*-arsono-*N*-phenylglycinamide.

Antimony. Dunning and Reid [68] have given improved directions for the preparation of stibanilic acid. Three series of azo

[62] Prescott and Hincke, *J. Am. Chem. Soc.*, **49**: 2744 (1927).
[63] Hamilton and Jelinek, *J. Am. Chem. Soc.*, **49**: 3165 (1927).
[64] Jurist and Christiansen, *J. Am. Chem. Soc.*, **50**: 191 (1928).
[65] Palmer and Scott, *J. Am. Chem. Soc.*, **50**: 536 (1928).
[66] Edee, *J. Am. Chem. Soc.*, **50**: 1394 (1928).
[67] Jacobs and Heidelberger, *Organic Syntheses*, **8**: 100 (1928).
[68] Dunning and Reid, *J. Am. Chem. Soc.*, **49**: 2869 (1927).

dyes containing antimony have been made and tested against trypanosomiasis in the white rat; that prepared from J-acid appears promising. It was found that the stibinic acid group not only dyes cotton directly but is more strongly auxochromic in character than the sulfonic acid group.

Chapter XXIII.

Sugar Chemistry.

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Preparative Methods. Glattfeld and Shaver [1] have reduced gluconic acid to glucose and galactonic acid to dulcitol by hydrogen and a platinum oxide catalyst, with moderate yields. Mannonic acid was only sparingly reduced.

New directions for the preparation of α-methylmannoside from vegetable ivory have been published by Hudson. [2]

The lactones of *l*-mannonic and *l*-gluconic acids were prepared by Upson, Sands and Whitnah [3] from *l*-arabinose by the cyanohydrin synthesis, with improved yield. The *l*-gluconic lactone was obtained crystalline for the first time and the *l*-mannonic lactone was obtained in two crystalline forms which are evidently structural isomers similar to those known for *d*-mannonic lactone.

Peterson and Spencer [4] give accurate directions for the preparation of pure crystalline cellobiose from its octaacetate by saponification with sodium ethylate followed by crystallization from glacial acetic acid.

Quick [5] recommends the use of borneol glucuronic acid for the preparation of the free acid in quantity; the conjugated acid is obtained by feeding borneol to dogs.

Certain of the penicillium organisms produce gluconic acid from glucose with yields as high as 62%. [6]

[1] Glattfeld and Shaver, *J. Am. Chem. Soc.*, **49**: 2305 (1927).
[2] Hudson, *Organic Syntheses*, **7**: 64 (1927).
[3] Upson, Sands and Whitnah, *J. Am. Chem. Soc.*, **50**: 519 (1928).
[4] Peterson and Spencer, *J. Am. Chem. Soc.*, **49**: 2822 (1927). The authors are apparently not familiar with the introduction of the use of sodium methylate for such saponifications by Zemplèn and the use of glacial acetic acid for sugar crystallizations by Phelps and the reviewer.
[5] Quick, *J. Biol. Chem.*, **74**: 331 (1927).
[6] May, Herrick, Thom and Church, *J. Biol. Chem.*, **75**: 417 (1927); Herrick and May, *ibid.*, **77**: 185 (1928).

Hydrolysis of Sugars. Carefully controlled experiments by Miller and Bandemer [7] show that acids adsorbed by ash-free charcoal are incapable of hydrolyzing sucrose. This novel result leads them to conclude that the adsorbed acids are in the undissociated state and that the adsorption does not imply a high concentration of hydrogen ions around the adsorbent as has often been assumed.

The accelerating influence of neutral salts on the rate of hydrolysis of sucrose by acids has been reinvestigated by Kautz and Robinson. [8]

Notes on the Clerget hydrolysis factor and a discussion of the method of double polarization in estimating sucrose have been published by Coates and Shen. [9]

Studies Relating to the Structures of the Sugars. Glattfeld and Woodruff [10] have prepared anew the two possible *d,l*-1,2-dihydroxybutyric acids and several of their derivatives to supply data needed in the study of the mechanism of saccharinic acid formation from the tetroses and other simple sugars.

Levene and Walti [11] have shown that both propylene oxide and glycidol condense through loss of water into substances of high molecular weight.

Evans and Cornthwaite [12] have shown that dihydroxyacetone in potassium hydroxide solutions reacts like glyceric aldehyde to give formic, acetic and lactic acids and pyruvic aldehyde, a result which is to be expected from the enediol theory of sugar rearrangements.

Evans and Hutchman [13] have studied the action of potassium hydroxide solutions on fructose from the standpoint of the enediol theory, which is confirmed by their results.

Hibbert and Burt [14] have drawn attention to the important rôle, in the case of dihydroxy-carbonyl derivatives, played by the hydroxyl groups in the γ,δ-positions to the carbonyl group and have obtained dehydrations and polymerizations of certain dihydroxyl ketones which appear analogous to the formation of polysaccharides, such as cellulose, from simple sugars.

[7] Miller and Bandemer, *J. Am. Chem. Soc.*, **49**: 1686 (1927).
[8] Kautz and Robinson, *J. Am. Chem. Soc.*, **50**: 1022 (1928).
[9] Coates and Shen, *Ind. Eng Chem.*, **20**: 70 (1928).
[10] Glattfeld and Woodruff, *J. Am. Chem. Soc.*, **49**: 2309 (1927).
[11] Levene and Walti *J. Biol. Chem.*, **75**: 325 (1927).
[12] Evans and Cornthwaite, *J. Am. Chem. Soc.*, **50**: 486 (1928).
[13] Evans and Hutchman, *J. Am. Chem. Soc.*, **50**: 1496 (1928).
[14] Hibbert and Burt, *J. Am. Chem. Soc.*, **50**: 1411 (1928).

Allison and Hixon [15] have reported various physical measurements which lead to the conclusion that glucose and other polyalcohols are intermediate in electron-sharing ability between typical radicals of the aliphatic and aromatic series.

Cameron [16] has shown that benzylamine and glucose in alcoholic solution with acetic acid form glucosebenzylamide, which passes in part at least to methylglyoxal.

New data on the catalysis of the mutarotation of glucose by acid and bases and an interpretation of the results through an extended conception of acids and bases acting as molecules rather than as ionized substances, have been published by Brönsted and Guggenheim.[17]

The oxidation of tetramethyl-γ-mannose by Levene and Meyer [18] has given a 10% yield of crystalline tetramethylmannonic lactone of the 1,4-ring structure, from which they conclude that at least a part of the sirupy tetramethyl-γ-methyl mannoside is a substance of this ring type.

Pentamethyl-d-mannose and pentamethyl-d-galactose have been prepared by Levene and Meyer,[19] who find them to have properties analogous to those reported for pentamethylglucose.

Levene and Meyer [20] have prepared two isomeric trimethyl- and tetramethylmethylglucosides.

Data on the rotatory dispersion of the mannose and glucose pentaacetates have been published by Levene and Bencowitz.[21]

Recent work by Schlubach and Huntenberg [22] has added two new pentabenzoates of glucose to the pair that has long been known,[23] and these four isomers, which are presumably alpha and beta forms of two ring structures, will doubtless become of first importance in the elucidation of the ring structures of the sugars. Levene and Meyer [24] have now carefully purified the four isomers by recrystallization and obtained rotations which in some cases are considerably different from those previously reported.

Levene and Wintersteiner [25] find that melibionic acid does not

[15] Allison and Hixon, *J. Am. Chem. Soc.*, **50**: 168 (1928).
[16] Cameron *J. Am. Chem. Soc.*, **49**: 1759 (1927).
[17] Brönsted and Guggenheim, *J. Am. Chem. Soc.*, **49**: 2554 (1927); *see also* Brönsted and Williams, *J. Am. Chem. Soc.*, **50**: 1338 (1928).
[18] Levene and Meyer, *J. Biol. Chem.*, **76**: 809 (1928).
[19] Levene and Meyer, *J. Biol. Chem.*, **74**: 695 (1927).
[20] Levene and Meyer, *J. Biol. Chem.*, **74**: 701 (1927).
[21] Levene and Bencowitz, *J. Biol. Chem.*, **74**: 153 (1927).
[22] Schlubach and Huntenberg, *Ber.*, **60B**: 1487 (1927).
[23] Fischer and Freudenberg, *Ber.*, **45**: 2709 (1912).
[24] Levene and Meyer, *J. Biol. Chem.*, **76**: 513 (1928).
[25] Levene and Wintersteiner, *J. Biol. Chem.*, **75**: 315 (1927).

form a stable lactone and conclude that the biose linkage is at carbon atom 4 of the glucose molecule. Galactoarabonic acid, from the degrading of lactose, forms two lactones in agreement with the view that the linkage in lactose is at carbon atom 4.

A study of the types of lactone formation shown by cellobionic acid and the glucoarabonic acid that may be prepared by degrading it has led Levene and Wolfrom [26] to the conclusion that the linkage in cellobiose is at the fourth carbon atom.

Wolfrom and Lewis [27] have contributed exhaustive experimental data which fully confirm the predictions of the enediol theory of sugar interconversion as applied to the methylated sugars. The mechanism of enol formation appears to be a tautomeric migration of a hydrogen atom rather than selective hydration and dehydration. No ketose sugars are formed by the action of dilute alkali on tetramethylglucose and the normal forms of tetramethylglucose and tetramethylmannose are found to be mutually interconvertible. They must therefore possess the same oxidic ring unless an improbable shifting of methyl groups occurs. This type of evidence promises to be of great value in correlating true epimeric forms of methylated sugars.

The pure alpha forms of fluoro-, chloro-, bromo-, and iodo-heptaacetylgentiobiose have been prepared by Brauns [28] and their rotations accurately measured. These conform with Brauns' view that the magnitude of the rotation is related to the atomic dimension of the halogen atom. He has succeeded in obtaining also the unstable beta forms of the chloro- and iodo-derivatives predicted by theory, in admixture with the stable alpha forms to which they rapidly change in solution, thus furnishing new experimental evidence that a Walden inversion occurs in the passage from a sugar acetate to the acetohalogen derivatives.

Miscellaneous. An interesting study of the accuracy to be obtained by the repetition of simple measurements, such as the reading of a sugar solution in a saccharimeter, has been made by Krogh,[29] who concludes that Lundsgaard and Holbøll have over-estimated the accuracy of the readings from which they inferred the existence of a new form of glucose in the blood.

The estimation of hydroxyl groups in sugars by treatment with

[26] Levene and Wolfrom, *J. Biol. Chem.,* **77**: 671 (1928).
[27] Wolfrom and Lewis, *J. Am. Chem. Soc.,* **50**: 837 (1928).
[28] Brauns, *J. Am. Chem. Soc.,* **49**: 3170 (1927).
[29] Krogh, *J. Biol. Chem.,* **74**: 393 (1927).

acetic anhydride and pyridine followed by titration gives good results.[30]

The action of fused caustic alkalies on glucose, fructose and cellulose results in the production of carbonates, methane and hydrogen, but with sucrose much free carbon was produced in addition.[31]

Voorhies and Alvarado [32] have published a preliminary paper suggesting the estimation of glucose by oxidation with iodine in alkaline solution, apparently without knowing that this procedure has been in wide use for many years.

Krieble, Skau and Lovering [33] have studied the influence of acidity, temperature and time on the extraction of the enzyme maltase from fresh and dried top yeast and their results will be most useful to those who desire to prepare this rather unstable enzyme. The use of maltase for the accurate estimation of maltose in mixtures of sugars is an attractive problem.

The appearance of a book by Waksman and Davison on enzymes,[34] published by the Williams and Wilkins Co., Baltimore, Md., may be mentioned.

[30] Peterson and West, *J. Biol. Chem.*, **74**: 379 (1927).
[31] Fry and Otto, *J. Am. Chem. Soc.*, **50**: 1138 (1928).
[32] Voorhies and Alvarado, *Ind. Eng. Chem.*, **19**: 848 (1927).
[33] Krieble, Skau and Lovering, *J. Am. Chem. Soc.*, **49**: 1728 (1927).
[34] Reviewed in *J. Am. Chem. Soc.*, **49**: 2341 (1927).

Chapter XXIV.

Nucleic Acids.

(July, 1926, to June, 1928)

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The publications dealing with the question of the structure of nucleic acids which have appeared are not numerous. The main progress has been made in the biochemical field. Until recently only one mononucleotide had been proved to exist in a free state in a tissue extract, namely, inosinic acid, which was discovered by Liebig in beef extract. Recently several nucleotides have been discovered in blood and in extracts of organs. These findings are important, not so much by themselves, but for the reason that they may serve as an indication of the distribution of the various nucleases in the organs. Those organs in which nucleotides remain intact are undoubtedly very poor in nucleotidases and perhaps in nucleosidases.

Another important discovery deals with the occurrence of a tetraribonucleotide in animal tissue. It had been accepted until recently that acids of this type are characteristic of the plant cell and it had been suggested that they be termed zymonucleic acids. It is now evident that both tetranucleotides, *i.e.,* that in which the carbohydrate component is *d*-ribose and that in which it is a hexose, occur in animal tissue.

Structure of the Nucleic Acid Molecule. The problems which have been discussed recently deal with the number of nucleotides which is contained in the molecule of ribonucleic acid. The question may be stated precisely as follows: Is uracil a pri-

mary or a secondary constituent of ribonucleic acid? This question has been the topic of discussion for over twenty years and it had finally been decided in favor of the primary origin of uracil. Steudel, who originally opposed the tetranucleotide structure of ribonucleic acid, later retracted his objections on the basis of work carried out by him in collaboration with Peiser. The method of investigation which led these authors to a revision of their original view consisted of a fractionation of the barium salts of the nucleotides. Calvery,[1] working under the direction of Jones, failed to corroborate the findings of Steudel and Peiser. He emphatically denied the correctness of the conclusions of the German workers and as emphatically endorsed the trinucleotide theory of the structure of nucleic acid, which had been advocated by Jones and Perkins.[2] Somewhat later, however, Calvery and Jones [3] published a second paper on the same subject. In this paper they explain their failure to detect uracil nucleotide among the products of hydrolysis of nucleic acid as being due to the fact that the lead salt of this nucleotide is more soluble in a solution of sodium acetate than the lead salts of the other nucleotides. Thus in the earlier experiment the lead salt of uracil nucleotide was lost. They therefore proceeded to hydrolyze ribonucleic acid by means of ammonia and, under these conditions, had no difficulty in isolating all four nucleotides. We add the conclusion of these authors without any comment on our part. "While we believe such to be true, nevertheless this article does not purport to prove that the molecule of yeast nucleic acid contains a uracil group. It shows that there is no experimental evidence to the contrary."

The question of the tetranucleotide structure of nucleic acids as well as the question of the mode of linkage of the individual nucleotides into a single molecule was the subject of a paper by Levene and Simms.[4] Their conclusion was drawn from a comparison of the titration curve of nucleic acid with a theoretical curve constructed on the basis of the dissociation constants of the mononucleotides. As an introduction to that investigation Simms and Levene [5] have developed a method for the graphical interpretation of electrometric titration data. The original should be consulted for details. By the application of this method to their

[1] Calvery, *J. Biol. Chem.*, **72**: 27 (1927).
[2] Jones and Perkins, *J. Biol. Chem.*, **62**: 557 (1924-25).
[3] Calvery and Jones, *J. Biol. Chem.*, **73**: 73 (1927).
[4] Levene and Simms, *J. Biol. Chem.*, **70**: 327 (1926).
[5] Simms and Levene, *J. Biol. Chem.*, **70**: 319 (1926).

analysis of the titration curve of ribonucleic acid the following conclusion was drawn as to the structure of the substance.

```
(6.0)
HO           (>13)
  >PO——Sugar——Adenine  (NH₂ = 3.7)
HO           |
(<2)         |
    (<2)     |     (>13)
    HO——PO——Sugar——Uracil  (OH = 10.2)
             |
             |
        (<2) |     (>13)          (NH₂ = 2.3)
        HO——PO——Sugar——Guanine  (OH = 10.1)
                 |
                 |
            (<2) |     (>13)
            HO——PO——Sugar——Cytosine  (NH₂ = 4.2)
```
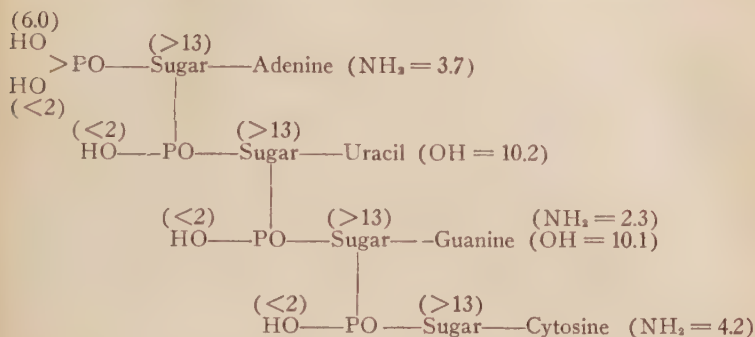
This figure signifies that the molecule of ribonucleic acid is a tetranucleotide in which the phosphoric acid radical of one nucleotide is linked to the sugar of another until a tetranucleotide is formed.

The last work dealing with the structure of nucleic acid is that of Calvery and Remsen,[6] which is concerned with the structure of triticonucleic acid. These authors isolated from the products of hydrolysis of this acid four mononucleotides, namely, guanosine-, adenosine-, cytidine-, and uridinephosphoric acids. By this finding they have established the identity of triticonucleic acid with the ribonucleic acid from other sources.

Nucleotides. There was no structural chemical work reported on this phase of the nucleic acid problem. On the other hand, many important contributions were made to the biochemistry of nucleotides. Reference to these will be made later in this article.

A contribution, however, was made by Buell and Perkins [7] to the method of preparation of guanosinephosphoric acid. The preparation of this nucleotide in crystalline form has always been a difficult matter because of the fact that slight impurity causes it to settle out in a gelatinous state. The authors prepare a silver salt of guanosinephosphoric acid, which is easily purified. This salt is then converted into the free nucleotide, which crystallizes with two molecules of water in the same manner as the crystalline guanylic acid obtained by Levene. There is a slight discrepancy in optical activity between the substance prepared by these writers

[6] Calvery and Remsen, *J. Biol. Chem.*, **73**: 593 (1927).
[7] Buell and Perkins, *J. Biol. Chem.*, **72**: 21 (1927).

and that prepared by Levene. However, the rotation of nucleotides, as well as of all other optically active electrolytes, is a function of the hydrogen ion concentration and the hydrogen ion concentrations may not have been identical in the solution of Buell and Perkins and in those of Levene. In a systematic study of the effect of ionization on optical rotation of nucleic acid derivatives, Levene, Simms and Bass [8] have shown that the rotation curves correspond with the titration curves.

Nucleosides. The problem of the structure of purine nucleosides may be regarded as completely solved by means of direct chemical methods. The structure of the pyrimidine nucleosides has been established only by indirect methods and therefore additional evidence in regard to the theory of their structure is always welcome. The problem under discussion is the linkage of the carbohydrate on the pyrimidine. It is assumed that position (3)

$$
\begin{array}{lll}
(1) & HN\!\!-\!\!CO & (6) \\
(2) & OC \quad\; CH & (5) \\
(3) & HN\!\!-\!\!CH & (4)
\end{array}
$$
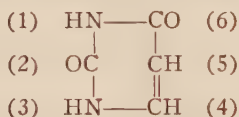
is the point of union of the sugar to the base.

Levene and Bass [9] have tested the action of hydrazine hydrate on uridine. The considerations which prompted them to apply this method were the following. Fosse, Hieulle, and Bass have shown that uracil is hydrolyzed by hydrazine into free urea and formyl-acetic acid, which combines with the hydrazine to form pyrazolone. Possibly the formation of pyrazolone is the primary reaction, the mechanism being the exchange of the hydrazine rest for the urea rest.

$$
\begin{array}{lllll}
(1) & HN\!\!-\!\!CO & (6) & NH_2 & HN\!\!-\!\!CO \quad\; NH_2 \\
(2) & OC \quad\; CH & (5) + & | \;\; = & | \quad\;\; CH + CO \\
(3) & HN\!\!-\!\!CH & (4) & NH_2 & HN\!\!-\!\!CH \quad\; NH_2
\end{array}
$$
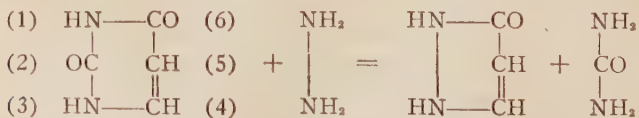
The reaction products can be isolated as xanthyl derivatives. In applying the reaction to uridine, if carbon (4) were substituted, a ribose-substituted pyrazolone and urea should be formed, and again both products might be isolated as xanthyl derivatives. If the sugar rest were in position (3), the products should be pyrazolone and urea riboside. The former could be isolated as the

[8] Levene, Simms and Bass, *J. Biol. Chem.*, **70**: 243 (1926).
[9] Levene and Bass, *J. Biol. Chem.*, **71**: 167 (1926-27).

xanthyl derivative, but urea riboside, on the other hand, in the presence of hydrazine would not form a xanthyl derivative. Hence, if the ribose in uridine is attached to the urea radical, from the products of the action of hydrazine hydrate only pyrazolone should be isolated as a xanthyl derivative. Such was actually the case.

Additional evidence in favor of the assumption of position (3) as the point of union between the two components of uridine and cytidine may be found in the physico-chemical properties of cytosine, which were investigated by Levene, Bass and Simms.[10] Cytosine was found on tautomerization to give two dissociation constants, one at pH 4.60 and the other at pH 12.16. Furthermore,

$$
\begin{array}{ccccc}
N\!\!=\!\!\!=\!\!C\!\!-\!\!NH_2 & & & N\!\!=\!\!\!=\!\!C\!\!-\!\!NH_2 \\
| \quad\quad | & & & | \quad\quad | \\
OC \quad\quad CH & \rightleftharpoons & HOC \quad\quad CH \\
| \quad\quad \| & & & \| \quad\quad \| \\
HN\!\!-\!\!\!-\!\!CH & & & N\!\!-\!\!\!-\!\!CH
\end{array}
$$

Kuhn and Sobotka have shown that glucosides have a dissociation constant at about pH 12. Then, if in cytidine the union between sugar and base were in position (4), cytidine should have two dissociation constants in the range of pH 12. Actually only one was found. This result strongly supports the view that in cytidine, and therefore in uridine also, the union between the two components is in position (3) of the pyrimidine. In the same paper the dissociation constants of several other pyrimidines were reported.

Thus the accumulated mass of indirect evidence speaks in favor of the assumption that position (3) of the pyrimidine is the point of linkage in the pyrimidine nucleosides.

Nitrogenous Constituents. The work on the nitrogenous constituents has little direct bearing on the structure of the nucleic acid molecule, but some of the findings may be useful for those who are interested in the synthetic side of the problem and others to those interested in the metabolism of nucleic acids in the body.

From the latter viewpoint Buell and Perkins [11] have made an important contribution by the discovery in pig serum of a purine which they seem to have identified as 2-hydroxy-6-aminopurine, an isomer of guanine. If the conclusion of these authors is substantiated, the substance will have to be regarded as an oxidation product of adenine and it would be an interesting case in which oxidation preceded deamination.

[10] Levene, Bass and Simms, *J. Biol. Chem.*, **70**: 229 (1926).
[11] Buell and Perkins, *J. Biol Chem.*, **72**: 745 (1927).

Uracil has been changed from a comparatively rare chemical into one which is easily available as a result of the simple preparation described by Davidson and Baudisch.[12] By treating a mixture of urea and malic acid with fuming sulfuric acid, uracil of a high degree of purity is obtained with a yield of 50-55%. The reaction involves an intermediate formation of oxymethyleneacetic acid from malic acid. In the same paper an excellent method is given for the preparation of 1.3-dimethyluracil by methylating uracil in aqueous solution with methyl sulfate and sodium hydroxide.

Baudisch and Davidson have continued their study of oxidation by complex iron salts. By oxidizing 5-aminouracil with potassium ferricyanide, they have obtained diuracilpyridazine.[13] In a study [14]

$$
\begin{array}{ccc}
HN\!-\!-\!CO & & OC\!-\!-\!NH \\
| \quad | & & | \quad | \\
OC \quad C\!-\!N\!=\!N\!-\!C & CO \\
| \quad \| & \| \quad | \\
HN\!-\!-\!C\!-\!-\!-\!-\!-\!C\!-\!-\!NH
\end{array}
$$
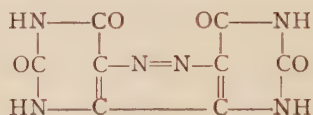
of the oxidation of hydantoin, isobarbituric acid and 5-aminouracil by sodium pentacyano-ammine-ferroate plus oxygen, they have shown that the rate of oxidation of the complex ion is inversely proportional to the pH of the solution; that the rate of catalyzed oxidation is greater in alkaline solution than in neutral; that pentacyano-ammine-ferroate and pentacyano-ammine-ferriate have identical catalytic activity. In a more recent paper [15] they have shown that the rate of oxidation of 5-substituted hydantoins is a function of the substituting group and that disubstitution in position (5) completely inhibits oxidation. It is evident that the point of attack in the hydantoin nucleus is at the (5) carbon. Since these oxidations occur, in general, only in alkaline solution, it is probable that oxidation is preceded by enolization. An isomeriza-

$$
\begin{array}{ccc}
HN\!-\!-\!CO & & HN\!-\!-\!COH \\
| \quad | & \rightleftharpoons & | \quad \| \\
OC \quad | & & OC \quad \| \\
| \quad | & & | \quad | \\
HN\!-\!-\!CHR & & HN\!-\!-\!CR
\end{array}
$$

tion of this type is impossible in the disubstituted hydantoins.

As stated under nucleosides, Levene, Bass and Simms [10] have determined by electrometric titration the dissociation constants of a number of pyrimidines: uracil, 1-methyluracil, 3-methyluracil,

[12] Davidson and Baudisch, *J. Am. Chem. Soc.*, **48**: 2379 (1926).
[13] Baudisch and Davidson, *J. Biol. Chem.*, **71**: 497 (1927).
[14] Baudisch and Davidson, *J. Biol. Chem.*, **71**: 501 (1927).
[15] Baudisch and Davidson, *J. Biol. Chem.*, **75**: 247 (1927).

4-methyluracil, 5-methyluracil, 1,3-dimethyluracil, dihydrouracil, cytosine and isocytosine.

Analytical Methods. Buell and Perkins [16] have developed a micronephelometric method for the quantitative determination of adenine nucleotide in blood. The method involves deproteinization of defibrinated blood with tungstic acid, precipitation of adenine nucleotide as the uranyl compound, liberation of adenine by hydrolysis with sulfuric acid, removal of uranium, precipitation of adenine as the silver compound and nephelometric comparison with a standard solution. Determinations of adenine nucleotide on a number of samples of blood have revealed large differences between certain species, *e.g.*, beef blood and pigeon blood. Adenine nucleotide is a constituent of red blood cells of many species, but it is doubtful that it occurs in white blood cells.

A microdetermination of the pentose in yeast nucleic acid and its derivatives, which gives accurate results with as little as 1 mg. of furfural, has been described by Hoffman.[17] The method consists of the quantitative conversion of the pentose into furfural by distillation with 20% hydrochloric acid and the quantitative colorimetric determination of the furfural in the distillate by means of aniline and acetic acid. The colorimetric determination is a modification of the method of Youngburg and Pucher. Under these conditions xylose and *d*-ribose are converted quantitatively into furfural in 3 hours, but arabinose requires 5 hours. Purine nucleotides also yield the theoretical amount of furfural in 3 hours, but pyrimidine nucleotides are so slowly hydrolyzed that it is impossible to obtain theoretical quantities of furfural from them. This fact makes possible a study of the pentose partition in yeast nucleic acid; since half the pentose is converted into furfural in 3 hours, the nucleic acid molecule is made up of equal numbers of purine groups and of pyrimidine groups.

Elek [18] has described a new microphosphorus determination which he has applied to various nucleic acid derivatives. The method, which requires 3-6 mg. of substance, consists of fusion of the substance with potassium nitrate and potassium hydroxide and determination of the phosphoric acid as ammonium phosphomolybdate.

16 Buell and Perkins, *J. Biol. Chem.*, **76**: 95 (1928).
17 Hoffman, *J. Biol. Chem.*, **73**: 15 (1927).
18 Elek, *J. Am. Chem. Soc.*, **50**: 1213 (1928).

.**Biochemical Investigations.** In this connection very important contributions have been made by Calvery.[19] Until recently the animal cell was differentiated chemically from the plant cell by the differences in their nucleic acids. The former contained the hexose nucleic acid, the latter, the ribose nucleic acid. Calvery has now succeeded in isolating from chicken embryos two nucleic acids: one has the properties of thymonucleic acid and the second those of ribonucleic acid. The separation of the two nucleic acids was brought about by separating the two parent substances, the α- and β-nucleoproteins. Of these, the former is coagulated by heat, while the second remains in solution. From the α-nucleoprotein the hexose nucleic acid has been isolated. The second nucleoprotein on partial hydrolysis yielded in crystalline form the four nucleotides, guanosine-, adenosine-, uridine- and cytidinephosphoric acids.

Calvery[20] also made another interesting contribution by isolating from tea leaves guanosine- and cytidinephosphoric acids. Both acids were isolated in crystalline form and both had the physical constants of the corresponding nucleotides isolated from ribonucleic acid. The isolation of adenosinephosphoric acid[21] from tea leaves by the same author has already been mentioned in the article on nucleic acids published in the first volume of this Survey. In this connection it may be mentioned that adenosinephosphoric acid has recently been isolated by Embden from muscle extract. The substance of Embden, which he regards as the precursor of inosinic acid, is not identical with the adenosinephosphoric acid isolated from nucleic acid. In the light of these observations it would be important to investigate the details of the structure of the nucleotides isolated from tea leaves. From a biological viewpoint the finding of Embden is of great importance, as it signifies that nucleotides have an independent function and are not merely decomposition products of nucleic acids.

[19] Calvery, *J. Biol. Chem.*, **77**: 489, 497 (1928).
[20] Calvery, *J. Biol. Chem.*, **72**: 549 (1927).
[21] Levene, *Survey of American Chemistry, I*: 169 (1926). In this review, this compound was incorrectly reported as adenine nucleoside instead of adenine nucleotide (*Cf.* Calvery, *J. Biol. Chem.*, **68**: 596 (1926).

Chapter XXV.

Biochemistry.

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Amino Acid Chemistry. A new reaction of primary amino acids with acetic anhydride in the presence of pyridine has been discovered independently by Levene and Steiger [1] and by Dakin and West.[2] CO_2 is evolved in the reaction and products are formed which are either crystalline or readily form crystalline derivatives. The reaction involves acetylation of the amino group and loss of the carboxyl group of the amino acid, with formation of an ultimate product, the properties of which are believed by Dakin and West to be best indicated by the formula $RCH(NHCOCH_3)-COCH_3$.

In studying the mechanism of the racemization of peptides and ketopiperazines, Levene and Steiger [3] have confirmed the observation of Levene and Pfaltz, that alkali racemizes the ketopiperazines but not the peptides. Ketopiperazines are theoretically capable of undergoing racemization by shift of one H from each asymmetric carbon to the adjacent CO group, as follows:
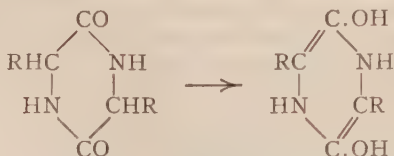
They find that when the theoretically labile H is replaced by an alkyl group, which would prevent enolization, no racemization occurs by alkali. The racemic change therefore appears attributable

[1] Levene and Steiger, *J. Biol. Chem.*, **74**: 689 (1927).
[2] Dakin and West, *J. Biol. Chem.*, **78**: 91 (1928).
[3] Levene and Steiger, *J. Biol. Chem.*, **76**: 299 (1928).

to action of alkali on the enol form, presumably accompanied by combination with the enol OH groups.

Vickery and Leavenworth[4] describe refinements in the preparation of arginine from protein hydrolysates by precipitation with Ag_2O at a pH of 10 to 11.

They have succeeded in preparing in the free form crystals of lysine,[5] an amino acid which had hitherto been crystallized only in its salts, and have improved the technique for preparing crystalline histidine and arginine.[6] They[7] have also improved the Kossel-Kutscher procedure for determining arginine, histidine and lysine in protein hydrolysates.

Amino Acid Physiology. Luck[8] finds that when equimolar amounts of various amino acids are fed to rats, mixed fractions of mono-amino and diamino acids increase the amino nitrogen content of the liver but only glycine increases the content of the muscles. No appreciable change in ammonia content of either liver or muscles occurs.

Bunney and Rose[9] find that rats maintain normal growth on diets free of arginine.

Wilhelmj and Bollman[10] find that intravenous injection into dogs of alanine, glycocoll, or phenylalanine produces an immediate rise in the rate of heat production, which requires several hours to return to basic level.

Luck, Morrison, and Wilbur[11] find that intravenous injection of insulin may lower the amino acid content of human blood by almost as great a proportion as it lowers the sugar content.

Johnston and Lewis[12] have studied the course of change in the urea nitrogen, amino acid nitrogen and undetermined non-protein nitrogen after ingestion of a series of amino acids.

Analytical Methods. Chiles[13] has described a procedure for direct nesslerization of the ammonia in the digest obtained in Kjeldahl nitrogen determination. He adds gum arabic to prevent precipitation of the $Hg-NH_3$ compound.

Elek[14] has improved the microtechnique for gravimetric deter-

4 Vickery and Leavenworth, *J. Biol. Chem.*, **75**: 115 (1927).
5 Vickery and Leavenworth, *J. Biol. Chem.*, **76**: 437 (1928).
6 Vickery and Leavenworth, *J. Biol. Chem.*, **76**: 701 (1928).
7 Vickery and Leavenworth, *J. Biol. Chem.*, **76**: 707 (1928).
8 Luck, *J. Biol. Chem.*, **77**: 13 (1928).
9 Bunney and Rose, *J. Biol. Chem.*, **76**: 521 (1928).
10 Wilhelmj and Bollman, *J. Biol. Chem.*, **77**: 127 (1928).
11 Luck, Morrison and Wilbur, *J. Biol. Chem.*, **77**: 151 (1927).
12 Johnston and Lewis, *J. Biol. Chem.*, **78**: 67 (1928).
13 Chiles, *J. Am. Chem. Soc.*, **50**: 217 (1928).
14 Elek, *J. Am. Chem. Soc.*, **50**: 1213 (1928).

mination of organic phosphorus. He destroys the organic matter by fusion with KOH and KNO_3 and weighs as ammonium phosphomolybdate.

Van Slyke, Hiller, and Berthelsen [15] have published microgasometric methods for iodates and sulfates, which they apply to the determination of total base in blood and urine, after conversion of all the mineral salts into sulfates. Iodate is estimated from the N_2 evolved by the reaction with hydrazine: $2NaIO_3 + 3N_2H_4 = 2NaI + 3N_2 + 6H_2O$. Alkali sulfates are converted into iodates by shaking with barium iodate, which is sufficiently more soluble than $BaSO_4$ to effect double decomposition: $Na_2SO_4 + Ba(IO_3)_2 = 2NaIO_3 + BaSO_4$. The iodate that goes into solution is determined as a measure of the amount of alkali sulfate.

Rothwell [16] shows that calcium can be determined in oxalated blood by precipitating the proteins with trichloroacetic acid, which is so strong an acid that it keeps the Ca in solution. Neutralization of the filtrate precipitates the calcium as oxalate.

Lactic acid determination in blood has been studied in detail by Ronzoni and Wallen-Lawrence [17] They find that adsorption of lactic acid by protein precipitates occurs but precipitation at pH 7.4 permits 94% to pass into the filtrate.

Iron is determined in tissues by Kennedy [18] by wet ashing with a mixture of sulfuric and perchloric acids, followed by colorimetric determination of iron as the sulfocyanate. Iron in solutions of blood ash is determined by King and Howard [19] by electrometric titration.

Glucose is estimated by Kingsbury [20] by taking advantage of the fact that it catalyzes the formation of "formose" from formaldehyde, and thus multiplies the reducing effect of the original glucose solution.

Harnes [21] simplifies the micro determination of lipoid phosphorus in blood by drying the sample on filter paper, extracting the lipoids with chloroform and determining the PO_4 in the extract by Briggs' method.

Kuttner and Cohen [22] have modified the Bell-Doisy-Briggs colorimetric micro method for phosphoric acid by substituting

[15] Van Slyke, Hiller and Berthelsen, *J. Biol. Chem.*, **74**: 659 (1927).
[16] Rothwell, *J. Biol. Chem.*, **74**: 257 (1927).
[17] Ronzoni and Wallen-Lawrence, *J. Biol. Chem.*, **74**: 363 (1927).
[18] Kennedy, *J. Biol. Chem.*, **74**: 385 (1927).
[19] King and Howard, *J. Biol. Chem.*, **75**: 27 (1927).
[20] Kingsbury, *J. Biol. Chem.*, **75**: 241 (1927).
[21] Harnes. *J. Biol. Chem.*, **77**: 405 (1928).
[22] Kuttner and Cohen, *J. Biol. Chem.*, **75**: 517 (1927).

stannous chloride in place of hydroquinone as reducing agent for the phosphomolybdic acid. They have applied the method to a microestimation of calcium, in which the PO_4 of precipitated calcium phosphate is determined.

Pucher and Finch [23] have determined the reduction values of glucose, fructose, galactose, xylose, arabinose, lactose and maltose, by the Hagedorn-Jensen, Benedict-Myers, and Folin-Wu blood sugar methods.

Benedict [24] has produced another modification of the Folin-Wu blood sugar method, in which the cuprous salt, produced by reduction of the cupric salt with sugar, is measured by means of the blue color produced when the cuprous salt reduces molybdic acid. Benedict's modified reagent indicates only 10-15 mg. of nonfermentable sugar, compared with the 25-30 mg. given by the accepted blood sugar methods, and therefore appears to be more specific for glucose.

Folin [25] in the meantime has abandoned his own copper-molybdic acid procedure in favor of a colorimetric modification of the ferricyanide reduction procedure introduced into blood chemistry by Hagedorn and Jensen. Folin converts the ferrocyanide, produced by reduction with sugar, into Prussian blue by acidification and determines it colorimetrically. One tenth of a cubic centimeter of blood suffices for duplicates by this method.

Levy and Doisy [26] find that borate retards the rate of oxidation of sugars by copper solutions; borate must accordingly be kept out of solutions for sugar analysis.

Dihydroxyacetone in blood and urine is determined by McClellan [27] by means of its ability to reduce directly the Folin-Wu phosphomolybdate reagent, the reduced reagent being titrated with permanganate.

Luck [28] has improved the technique of preparing tissue extracts for determination of their amino acids. He freezes the tissues with liquid air, extracts with ice water, coagulates with heat and acetic acid and treats the filtrate with infusorial earth. Kiech and Luck [29] find that Folin's tungstic acid reagent also serves well for removal of proteins from the extract. In the filtrate not only amino

[23] Pucher and Finch, *J. Biol. Chem.*, 76: 331 (1928).
[24] Benedict, *J. Biol. Chem.*, 76: 457 (1928).
[25] Folin, *J. Biol Chem.*, 77: 421 (1928).
[26] Levy and Doisy, *J. Biol. Chem.*, 77: 733 (1928).
[27] McClellan, *J. Biol. Chem.*, 76: 481 (1928)
[28] Luck, *J. Biol. Chem.*, 77: 1 (1928).
[29] Kiech and Luck, *J. Biol. Chem.*, 77: 723 (1928).

N but also urea can be determined, the latter by the gravimetric method of Fosse, as the dixanthydryl compound.

Bloor [30] has modified his blood lipoid method by abandoning the nephelometric estimation of the extracted lipoids and applying Bang's procedure, in which the material is oxidized with dichromate and sulfuric acid and is estimated from the amount of dichromate reduced.

Aldrich and Bledsoe [31] have applied the Pettenkoper reaction to the quantitative determination of bile acids in blood.

Myers and Muntwyler [32] have applied the Clark indicator series to pH determination in urine with the Myers' biocolorimeter.

Fenn [33] describes a micromethod for simultaneous determination of CO_2 produced and O_2 used by small amounts of living material. The CO_2 is absorbed by barium hydroxide solution and measured by the fall in conductivity. The O_2 is estimated from decrease in gas volume.

Bacterial Chemistry. Anderson [34] has continued the studies of the organic constituents of the tubercle bacillus that have been in progress at the Yale laboratory. He has separated the waxes, glycerides and phosphatides, the latter in large amounts ; also organic bases and a polysaccharide. A phosphatide fraction was hydrolyzed, and yielded palmitic and oleic acids, glucose, a sugar acid and glycerophosphoric acid.

Heidelberger and Goebel [35] have continued their work on the organic constituents of the different pneumococci. They find that the saccharide, aldobionic acid, formerly isolated by them from Pneumococcus III, is a glucoside compound of glucose and glucuronic acid. From Friedländer's bacillus Goebel [36] isolated a polysaccharide composed of 2 molecules of an isomer of the above aldobionic acid and 1 molecule of glucose.

Blood Physical Chemistry. Loeb and Nichols [37] have studied the equilibrium of calcium between serum in a collodion sac and a dialysate outside. From the fact that a greater concentration of Ca remains in the sac than that calculated from Donnan's law on the assumption of complete dissociation, they decide that a fraction (up to 40%) of the Ca in the serum is bound in

[30] Bloor, *J. Biol. Chem.*, **77**: 53 (1928).
[31] Aldrich and Bledsoe, *J. Biol. Chem.*, **77**: 519 (1928).
[32] Myers and Muntwyler, *J. Biol. Chem.*, **78**: 225 (1928).
[33] Fenn, *Am. J. Physiol.*, **84**: 110 (1928).
[34] Anderson, *J. Biol. Chem.*, **74**: 525, 537 (1927).
[35] Heidelberger and Goebel, *J. Biol. Chem.*, **74**: 613 (1927).
[36] Goebel, *J. Biol. Chem.*, **74**: 619 (1927).
[37] Loeb and Nichols, *J. Biol. Chem.*, **74**: 645 (1927).

undissociated compounds. Previous dialysis to remove other crystalloids, or extraction with ether, did not affect this property of serum: it is concluded that the non-dissociating Ca is practically all bound to protein.

Stadie and Hawes [38] have studied most completely the question of the validity of electrometric pH determinations in hemoglobin solutions and conclude that they are entirely valid. These authors confirm Hastings and Sendroy [39] in showing that hemoglobin lowers the pK' constant of the Hasselbalch equation, and show that the lowering is a linear function of the hemoglobin concentration. The value of pK' in hemoglobin solutions is indicated by the equation $pK' = pK - (0.54 - m[Hb])\sqrt{\text{ionic strength}}$ where pK is the negative log of the first dissociation constant of carbonic acid in the absence of other solutes. The equation also holds for solutions of methemoglobin, cyanhemoglobin and nitric oxide hemoglobin, each with characteristic m values. The pK' for red blood cells is estimated to be 5.98 when the hemoglobin is oxygenated, 5.87 when it is reduced. Stadie [38] discusses the application of the Debye-Hückel theory to solutions of hemoglobin in $NaCl$ and $NaHCO_3$.

L. J. Henderson, Bock, Dill, and their collaborators have continued their studies on the physical chemistry of the blood of subjects in various physiological states [40] and have extended their work to the blood of terminal uremia.[41] The latter shows extraordinary abnormalities, pH below 7, bicarbonate and hemoglobin greatly reduced, and, as would be expected from the lowered pH, a marked lessening of the differences in Cl and HCO_3 concentration between cells and plasma. The entire picture is one of blood in which the margins of ability to carry O_2 and CO_2 and to buffer invading acids have been wiped out: only enough is left to maintain life at a minimum rate, and further decrease is fatal. In similar studies of the blood in pernicious anemia,[42] a somewhat decreased affinity of the hemoglobin for O_2 at a given CO_2 tension are noted, together with other abnormalities.

Cullen and Earle [43] find that the quinhydrone electrode used for

[38] Stadie and Hawes, *J. Biol. Chem.*, **77**: 241, 265 (1928); Stadie, *ibid.*, **77**: 303 (1928).
[39] Hastings and Sendroy, *J. Biol. Chem.*, **65**: 445 (1925).
[40] Dill, Hurxthal, Van Caulaert, Fölling and Bock, *J. Biol. Chem.*, **74**: 303 (1927); Dill, Lawrence, Hurxthal and Bock, *J. Biol. Chem.*, **74**: 313 (1927).
[41] Henderson, Bock, Dill, Hurxthal and Van Caulaert, *J. Biol. Chem.*, **75**: 305 (1927).
[42] Dill, Bock, Van Caulaert, Fölling, Hurxthal and Henderson. *J. Biol. Chem.*, **78**: 191 (1928).
[43] Cullen and Earle, *J. Biol. Chem.*, **76**: 565 (1928).

determination of plasma pH gives results consistently 0.06 pH more acid than those by the H_2 electrode. Determinations on the serum of a series of students [44] gave plasma pH values between 7.41-7.50, H_2 electrode standard. The fact that these results are somewhat higher than usual may have been due to hyperventilation caused by hot weather.

Carbohydrate Metabolism. The Coris [45] have continued their brilliant study of intermediate carbohydrate metabolism. They find that absorption of the different sugars, fed separately, proceeds for each at a characteristic maximum rate, attained when relatively small amounts are fed. When more is consumed, absorption does not go faster; it continues longer. When a mixture of sugars, or sugar and amino acids is fed, each partially inhibits the absorption of the others.

Deuel, Ellis, Wilson, and Milhorat, [46] by exhaustive studies of the gas metabolism and sugar balance in phlorhizinized dogs, some of whom had had their kidneys removed, have shown that phlorhizin does not deprive the tissues of their power to burn glucose. The reason why phlorhizin ordinarily stops glucose combustion is that it stimulates renal glycosuria to such an extent that the glucose supply is speedily removed from the body.

Hoskins and Snyder [47] record the fact that insulin injected intraperitoneally into rabbits may fail to cause hypoglycemia. Sahyun and Blatherwick, [48] however, find that if the injection is repeated the fall in blood sugar is comparable to that after intravenous injection. The failure of the first intraperitoneal injection to act is an unexplained phenomenon.

Sugar injected intravenously into animals was traced to the tissues by analyses of the latter by Folin, Trimble, and Newman. [49] The sugar concentration in the muscles was always much less than in the blood; in the skin the concentration was about equal to that in the blood. Of sucrose injected into guinea pigs, all could be recovered, and of glucose the greater part. Glycogen formation in muscles was found to be so slow in anesthetized dogs that increase in the glycogen content could hardly be determined half an hour after the injection.

[44] Cullen and Earle, *J. Biol. Chem.*, **76**: 583 (1928).
[45] Cori and Cori. *J. Biol. Chem.*, **74**: 473 (1927); **76**: 755 (1928).
[46] Deuel, Ellis, Wilson and Milhorat, *J. Biol. Chem.*, **74**: 265 (1927).
[47] Hoskins and Snyder, *J. Biol. Chem.*, **75**: 147 (1927).
[48] Sahyun and Blatherwick, *J. Biol. Chem.*, **77**: 459 (1928).
[49] Folin, Trimble and Newman, *J. Biol. Chem.*, **75**: 263 (1927).

Chaikoff and Weber [50] from McLeod's laboratory, have con-
tributed to the question concerning the possibility of carbohydrate
formation from fatty acids in the body, a series of experiments on
depancreatized dogs injected with epinephrine. These animals ex-
creted more glucose than appeared possible to account for from
the glycogen content of the body, the sugar derivable from
catabolized protein and from the glycerol of the fats burned. The
authors believe, therefore, that there must have been formation
of sugar from fatty acids.

Ariyama [51] in Shaffer's laboratory has shown that action of
liver hash on glucose phosphate yields methylglyoxal to as much
as 10% of the theoretical maximum, indicating that methylglyoxal
may be an intermediary step in lactic acid formation from hexose.

Somogyi [52] has for the first time determined the fermentable
sugar in both cells and serum of human blood. He finds that
although, as shown by previous authors, the total copper-reducing
material per 100 cc. is about equal in cells and serum, about 40 mg.
per 100 cc. of the reducing substance determined in the cells is
non-fermentable, and certainly not glucose, while in the serum
such material accounts for reducing power equivalent to only about
8 mg. of glucose per 100 cc.

Soskin [53] confirms a conclusion reached by Bollman, Mann, and
Magath, that muscle glycogen is not available as a source of blood
sugar in the absence of the liver. Adrenalin injection, ether
anesthesia and asphyxia, which cause increase in blood sugar in
normal dogs, do not even prevent the fall in blood sugar in
eviscerated animals.

Enzymes. Sherman [54] has continued his studies of pancreatic
amylase action. He finds that the optimum pH varies markedly
with the temperature when the enzyme acts in phosphate mixtures
but not in acetate. Otherwise, different buffers in equivalent
amounts appeared to have little difference in effect on amylase
activity.

Raymond and Winegarden [55] have advanced the procedure for
the purification of cozymase, and have developed a conductivity
method for determining CO_2 evolved from fermenting mixtures.

[50] Chaikoff and Weber, *J. Biol. Chem.*, **76**: 813 (1928).
[51] Ariyama, *J. Biol. Chem.*, **77**: 359 (1928).
[52] Somogyi, *J. Biol. Chem.*, **78**: 117 (1928).
[53] Soskin, *Am. J. Physiol.*, **81**: 382 (1927).
[54] Sherman Caldwell and Adams, *J. Am. Chem. Soc.*, **49**: 2000 (1927); Sherman,
Caldwell and Dale, *Ibid.*, **49**: 2596 (1927).
[55] Raymond and Winegarden, *J. Biol. Chem.*, **74**: 175, 189 (1927).

A urease preparation in crystalline form, 730 times more active than the jack bean meal from which it was prepared, is described by Sumner and Hand.[56]

Geddes and Hunter [57] have studied the kinetics of yeast asparaginase, which splits ammonia from the amide group of asparagin. The optimum pH is 8.0. The course of reaction is expressed by the equation $Kt = m \log \dfrac{a}{a+x} + X$, which has previously been found to apply to urease, invertase, and some other enzymes. Of a number of other amides tested, only that of glutaminic acid was attacked by the enzyme. A similar but less active asparaginase preparation was prepared from calf liver.

Falk's studies of the lipases of tissues have been extended with his collaborators, Noyes and Lorberblatt,[58] in studies of the trout at different ages.

Harvey [59] has determined the amount of oxygen utilized per light unit emitted by the luciferin of *Cypridina* in the presence of luciferase. He concludes that the reaction is: luciferin $+ 1/2 O_2 =$ oxyluciferin $+ H_2O + 54$ Cal., and that 1% of the energy evolved is in the form of light, 99% in the form of heat.

Hemoglobin Regeneration. Whipple and Robscheit-Robbins [60] have continued their studies of factors determining the rate of hemoglobin regeneration from severe anemia caused by bleeding dogs. They find that when hemoglobin itself is fed by mouth to such anemic dogs, from 5 to 20% is used for construction of blood hemoglobin. When a pancreatic digest of hemoglobin is given 40% may be thus used. When intact hemoglobin is injected intravenously or intraperitoneally 80% may be used. When iron salts plus liver or kidney are fed the rate of hemoglobin regeneration represents the sum of the effects of feeding the two separately. It appears therefore that the effect of liver or kidney feeding is not due solely to the iron or ash content of these organs, but to a combined effect of the ash and some organic constituent.

Cohn, Minot, Alles, and Salter [61] have separated in a highly active, if not yet chemically pure, state the organic substance in liver which, when fed to patients with pernicious anemia, causes them to regenerate hemoglobin. The active material contains 19%

[56] Sumner and Hand, *J. Biol. Chem.*, **76**: 149 (1928).
[57] Geddes and Hunter, *J. Biol. Chem.*, **77**: 197 (1928).
[58] Falk, Noyes and Lorberblatt, *J. Gen. Physiol.*, **10**: 837 (1927).
[59] Harvey, *J. Gen. Physiol.*, **10**: 875 (1927).
[60] Whipple and Robscheit-Robbins, *Am. J. Physiol.*, **83**: 60. 76 (1927).
[61] Cohn, Minot, Alles and Salter, *J. Biol. Chem.*, **77**: 325 (1928).

N, is precipitated by phosphotungstic acid and has the character of a polypeptide.

Waddell, Elvehjem, Steenbock, and Hart [62] find that rats, suffer- ing from nutritional anemia brought on by a diet of cows' milk, can be speedily cured by feeding ashed residues of liver, lettuce and yellow corn, or their acid extracts, in such an amount that 0.5 mg. of Fe is provided daily. However, 0.5 mg. of Fe in various pure salts has no effect at all. In order to make the Fe effective, a small proportion of *copper* salt, similar to the proportion found in liver ash, must be added.[63] The nutritional anemia cured by Hart and his collaborators differs from the pernicious anemia studied by Cohn, Minot and their collaborators, in that the former is a condition with unimpaired hemoglobin-forming mechanism, and the only requirement for cure is materials to build the sub- stance. In pernicious anemia the mechanism itself is so retarded that stimulus to it, as well as an adequate supply of hemoglobin building materials, is required.

Lipoid Chemistry. Levene and Rolf [64] have improved the method for preparing cephalin from brain tissue. Levene and Landsteiner [65] have isolated from horse kidneys a lipoid which on hydrolysis yields sphingosine, fatty acids and a sugar, probably galactose.

Lipoid Physiology. Anderson and Mendel [66] have shown in rats the manner in which the chemical nature of the body fat follows that of food fat. Theis [67] finds that insulin injection, at the peak of its effect, reduces the ratio, phospholipid : neutral fat, in the liver. Bloor, Gillette, and James [68] have reproduced in par- tially depancreatized dogs a lipemia similar to that of severe human diabetes, have studied the changes in the different lipoid fractions and the effects of diet.

Mineral Metabolism. Shohl and Bennett [69] find by experi- ments on puppies that the degree of negative phosphorus balance affords a quantitative measure of the rickets-producing property of the regime. St. John [70] finds that the diet of rats must contain 0.3% of Na to produce normal growth. Shelling, Kramer, and

[62] Waddell, Elvehjem, Steenbock and Hart, *J. Biol. Chem.*, **77**: 777 (1928).
[63] Hart, Steenbock, Waddell and Elvehjem, *J. Biol. Chem.*, **77**: 797 (1928).
[64] Levene and Rolf, *J. Biol. Chem.*, **74**: 713 (1927).
[65] Levene and Landsteiner, *J. Biol. Chem.*, **75**: 607 (1927).
[66] Anderson and Mendel, *J. Biol. Chem.*, **76**: 729 (1928).
[67] Theis, *J. Biol. Chem.*, **77**: 75 (1928).
[68] Bloor, Gillette and James, *J. Biol. Chem.*, **75**: 61 (1927).
[69] Shohl and Bennett, *J. Biol. Chem.*, **76**: 633 (1928).
[70] St. John, *J. Biol. Chem.*, **77**: 27 (1928).

Orent [71] have found that, for calcification of cartilage *in vitro*, the pH of normal serum is the most favorable reaction. Magnesium retards calcification *in vitro*.

Organic Phosphorus Compounds. Fiske and Subbarow [72] appear to have solved the nature of the manner in which the large amounts of creatine exist in muscle and the probable function of the compound. They find that the creatine is combined with 1 molecule of phosphoric acid, by a phosphamine linking:

$$HN=C<^{NH-PO-(OH)_2}_{N(CH_3).CH_2.COOH}.$$

The acid compound is stable in the form of dibasic alkali salt, in which it exists at neutral reaction but hydrolyzes instantly when slightly acidified. Such hydrolysis may occur when lactic acid accumulates in muscle. In this case the B_2HPO_4 formed by the hydrolysis would act as buffer and limit the development of acidity. Irving and Wells [73] find that in extracts of muscle made with acidified ice water a large part of the inorganic P is in an unstable form, behaving like Fiske and Subbarow's phosphocreatine.

Organic Structure of Plant Substances. Jacobs and Gustus [74] have continued their studies of the organic structure and related biologic properties of the cardiac glucosides. The work is too extensive to be adequately discussed here.

Proteins. Levene and Bass [75] find that treatment of gelatin with 0.1 to 1.0 N alkali racemizes some of the constituent amino acids, whereas treatment with 3.0 N alkali does not. Apparently racemization occurs in the unhydrolyzed protein, and when the stronger alkali is used hydrolysis occurs before there is time for racemization. Similar studies of casein [76] indicated that in this protein also racemization precedes hydrolysis.

Jones and Gersdorff, and Csonka have carried on their problem of isolating and determining the properties and amino acid composition of vegetable proteins, in continuance of the famous work of T. B. Osborne. They have isolated and analyzed the globulins [77] and glutelin [78] of rice, the glutelin of oats [79] and the proteins of sesame seed.[80]

[71] Shelling, Kramer and Orent, *J. Biol. Chem.*, **77**: 157 (1928).
[72] Fiske and Subbarow, *Science*, **67**: 169 (1928).
[73] Irving and Wells, *J. Biol. Chem.*, **77**: 97 (1928).
[74] Jacobs and Gustus, *J. Biol. Chem.*, **74**: 787, 795, 805, 811, 829 (1927).
[75] Levene and Bass, *J. Biol. Chem.*, **74**: 715 (1927).
[76] Levene and Bass, *J. Biol. Chem.*, **78**: 145 (1928).
[77] Jones, Gersdorff and Csonka, *J. Biol. Chem.*, **74**: 415 (1927).
[78] Jones and Csonka, *J. Biol. Chem.*, **74**: 427 (1927).
[79] Csonka, *J. Biol. Chem.*, **75**: 189 (1927).
[80] Jones and Gersdorff, *J. Biol. Chem.*, **75**: 213 (1927).

The hemocyanin of the horseshoe crab, *Limulus polyphemus,* has been prepared by Redfield, Coolidge, and Shotts.[81] It contains 0.173% of Cu and 17.3% of N. It is different from the hemocyanin of the octopus and snail. In hemocyanins from 9 animals Redfield, Coolidge, and Montgomery [82] found that 1 molecule of O_2 is combined reversibly for each atom of Cu present.

Redfield and Mason [83] find that the maximal acid-combining capacity of the hemocyanin of *Limulus* agrees closely with that calculated from the dibasic amino acids of the protein.

Conant and Scott [84] have studied the equilibrium between methemoglobin, with its iron in the ferric state, and ordinary hemoglobin, with its iron in the ferrous state, under the influence of a series of oxidizing agents. They describe a new method for determination of methemoglobin [85] in which it is reduced to ordinary hemoglobin by stannous chloride, and the oxygen combining capacity of the hemoglobin thus regenerated is determined by the Van Slyke-Neill method.

Northrop and Kunitz [86] have continued their studies of the factors which determine the swelling of gelatin in water. They find that qualitatively and quantitatively the swelling of isoelectric gelatin conforms to the assumption that gelatin consists of a network of relatively insoluble material containing a solution of a more soluble form of gelatin. "Water enters owing to the osmotic pressure of the soluble material and thereby puts the network under elastic strain. The process continues until the elastic force equals the osmotic pressure." Applying his results to biological material Northrop [87] concludes that the rate of swelling of *Arbacia* eggs in sea water may be expressed by the formulæ derived for the rate of increase in volume of a solution enclosed in a collodion sac; while the swelling of slices of carrots in distilled water follows the equation for the swelling of similarly shaped blocks of gelatin.

Pertzoff [88] in the laboratory of E. J. Cohn estimates the combining weight of casein with alkali as the grams of casein dissolved by a gram equivalent of alkali. He finds that between 21° and 37° the combining weight is 2100. Rise of temperature to 60°

[81] Redfield, Coolidge and Shotts, *J. Biol. Chem.,* **76**: 185 (1928).
[82] Redfield, Coolidge and Montgomery, *J. Biol. Chem.,* **76**: 197 (1928).
[83] Redfield and Mason, *J. Biol. Chem.,* **77**: 451 (1928).
[84] Conant and Scott, *J. Biol. Chem.,* **76**: 207 (1928).
[85] Conant, Scott and Douglass, *J. Biol. Chem.,* **76**: 223 (1928).
[86] Northrop and Kunitz, *J. Gen. Physiol.,* **10**: 905 (1927); Northrop, *ibid.,* **10**: 893 (1927).
[87] Northrop, *J. Gen. Physiol.,* **11**: 43 (1927).
[88] Pertzoff, *J. Gen. Physiol.,* **10**: 961 (1927).

increases it gradually to 3700, at which level it stays constant from 60° to 85°. The combination with alkali appears to be in stoichiometric proportions. The paracasein [89] formed by the action of rennin on casein has a combining weight 2/3 that of casein. The solubility at 5° of both casein and paracasein in isoelectric condition is 0.70 mg. N per 100 gm. of water. Further experiments [90] emphasize the genuine nature of the chemical difference between casein and paracasein by showing that the combining weights of each for alkali remain characteristic after various chemical treatments.

Stearn,[91] from a study of the conductivity curves of gelatin to which increments of alkali are added, concludes that the alkali is nearly all bound by a process of chemical salt formation, the proportion adsorbed being small.

Purines. Harding, Allin, and Eagles [92] have demonstrated an increased blood uric acid content, with decreased uric acid excretion, as the result of high fat diets.

Buell and Perkins [93] have devised a nephelometric method for determination of adenine nucleotide in blood. They find 10 to 30 mg. per 100 cc. in the blood of man, and varying amounts in other animals.

Calvery [94] has isolated from chicken embryos a nucleoprotein which yields on hydrolysis all 4 of the nucleotides obtained by Levene, Jacobs, and La Forge from yeast nucleic acid; also a hexose nucleic acid similar to that previously obtained from animal tissues.[95]

Cerecedo [96] has studied the fate of pyrimidines fed to dogs. Uracil and thymine are converted into urea. Cytosine and 5-methylcytosine are partly excreted unchanged, partly deaminized to uracil and thymine respectively.

Radiation Physiology. Hess and Anderson [97] find that three sitosterols isolated from corn oil all acquire intense antirachitic properties when irradiated with ultraviolet light.

Yoder [98] finds that irradiation of rachitic rats increases absorption of phosphate and calcium from the intestine. The pH of the

[89] Pertzoff, *J. Gen. Physiol.,* **10:** 987 (1927).
[90] Pertzoff, *J. Gen. Physiol.,* **11:** 239 (1928).
[91] Stearn, *J. Gen. Physiol.,* **11:** 377 (1928).
[92] Harding, Allin and Eagles, *J. Biol. Chem.,* **74:** 631 (1927).
[93] Buell and Perkins, *J. Biol. Chem.,* **76:** 95 (1928).
[94] Calvery, *J. Biol. Chem.,* **77:** 489 (1928).
[95] Calvery, *J. Biol. Chem.,* **77:** 497 (1928).
[96] Cerecedo, *J. Biol. Chem.,* **75:** 661 (1927).
[97] Hess and Anderson, *J. Biol. Chem.,* **74:** 651 (1927).
[98] Yoder, *J. Biol. Chem.,* **74:** 321 (1927).

intestinal tract below the duodenum was lowered: presumably the increased calcium and phosphate absorptions were connected with increased solubility in the more acid intestinal contents.

On the other hand, in a human subject, on an acidotic, calcium-deficient diet, Hart, Tourtellotte, and Heyl [99] could find no increase in retention of Ca, Mg or PO_4 as the result of direct radiation for 20 days.

Sulfur Compounds. du Vigneaud [100] presents evidence that the sulfur of insulin is in the form of cystine.

Johnson and Voegtlin [101] have improved the method for preparation of glutathione, have determined the optical rotation of the substance dissolved in 10% HCl to be 80-94° and have described the copper, gold, and lead compounds.

Tissue Metabolism. Fenn [102] has devised micro apparatus for determining CO_2 formed and O_2 utilized by isolated nerve tissues. He has found the quotient, (CO_2 evolved) : (O_2 absorbed), of the resting nerve to be 0.97, while the quotient of the excess gas exchange caused by stimulus averaged 1.19.

Himwich and Castle [103] have determined the quotient, (CO_2 evolved) : (O_2 absorbed), in dog muscles by gas analyses of the arterial and venous blood. The value of the quotient was found between 0.71 and 0.77. Had only fat been utilized it would be 0.70, while carbohydrate alone would give 1.00. It appears that the resting muscles do not burn exclusively carbohydrate but to a large extent also fat.

Hayman and Schmidt [104] have similarly determined the gas exchange of dogs' kidneys. They noted a tremendous variation in O_2 consumption, from 0.009 to 0.113 cc. per gram per minute. The higher figures accompanied greater blood flow and more profuse diuresis. The difference in energy utilization between rest and activity appears almost as great in the kidney as in muscles.

Vitamin A. (*Growth Promoting.*) Supplee and Dow [105] find that milk can be irradiated to give it antirachitic properties without destroying its efficiency in promoting growth of rats. Heller [106] finds that light is the chief factor in the production of vitamin A in seedlings. Vitamin B did not appear to be formed in plants

99 Hart, Tourtellotte and Heyl, *J. Biol. Chem.*, **76**: 143 (1927).
100 du Vigneaud, *J. Biol. Chem.*, **75**: 393 (1927).
101 Johnson and Voegtlin, *J. Biol. Chem.*, **75**: 703 (1927).
102 Fenn, *J. Gen. Physiol.*, **11**: 175 (1927).
103 Himwich and Castle, *Am. J. Physiol.*, **83**: 92 (1927).
104 Hayman and Schmidt, *Am. J. Physiol.*, **83**: 502 (1928).
105 Supplee and Dow, *J. Biol. Chem.*, **75**: 227 (1927).
106 Heller, *J. Biol. Chem.*, **76**: 499 (1928).

until after the germination period, while vitamin C was formed even more rapidly than A. Evans [107] finds that diets deficient in vitamin A, when fed to female rats, diminish their fertility by causing failure of the sperm to become implanted on the ovum.

Vitamin B. (*Anti-neuritic and Growth Promoting.*) Sure [108] finds that lactation in rats is maintained by the vitamin B extracted with alcohol from wheat embryo. Sherman and Mac-Arthur [109] have defined conditions for quantitative estimation of vitamin B by its effect on growth of rats. Sherman and Gloy [110] find that a wide range of protein intake does not affect the vitamin B requirement. Sherman and Axtmayer [111] present evidence that the vitamin B of yeast is really a composite of at least two substances, both of which promote growth, but only one of which is antineuritic. They call these vitamins F and G. Salmon, Guerrant, and Hays,[112] Evans and Burr,[113] Hunt,[114] and Kennedy and Palmer [115] confirm the multiple nature of the yeast vitamins.

Sure [116] finds that it is easier to assure adequate vitamin B to suckling rats by direct feeding of yeast to them than by feeding it to the mothers.

Sweetman and Palmer [117] have introduced a novelty into the technique of vitamin testing by using the flour beetle, *Tribolium confusum,* in place of rats.

Evans and Burr [118] find that the effect of yeast in promoting lactation is due to the antineuritic component, not the growth-producing one, of the vitamin B.

Vitamin E. (*Reproduction.*) Sure [119] finds that both wheat oil and butter contain vitamin E, but the oil has more. Evans and Burr [120] describe paralysis in the suckling young rats of mothers deprived of Vitamin E.

[107] Evans, *J. Biol. Chem.,* **77**: 651 (1928).
[108] Sure, *J. Biol. Chem.,* **74**: 55 (1927).
[109] Sherman and MacArthur, *J. Biol. Chem.,* **74**: 107 (1927).
[110] Sherman and Gloy, *J. Biol. Chem.,* **74**: 117 (1927).
[111] Sherman and Axtmayer, *J. Biol. Chem.,* **75**: 207 (1927).
[112] Salmon. Guerrant and Hays, *J. Biol. Chem.,* **76**: 487 (1928).
[113] Evans and Burr, *J. Biol. Chem.,* **77**: 231 (1928).
[114] Hunt, *J. Biol. Chem.,* **78**: 83 (1928).
[115] Kennedy and Palmer, *J. Biol. Chem.,* **76**: 591 (1928).
[116] Sure, *J. Biol. Chem.,* **76**: 659 (1928).
[117] Sweetman and Palmer. *J. Biol. Chem.,* **77**: 33 (1928).
[118] Evans and Burr, *J. Biol. Chem.,* **76**: 263 (1928).
[119] Sure, *J. Biol. Chem.,* **74**: 71 (1927).
[120] Evans and Burr, *J. Biol. Chem.,* **76**: 273 (1928).

Chapter XXVI.

Foods.

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In the following survey of American chemical literature on foods, consideration is limited to work on such foods or food materials as are utilized as human foods. Further, no studies in the field of nutrition are reviewed, since such material is considered elsewhere in this volume. Even in the food analytical field, it has not seemed necessary to review in detail the progress which has been made, since such work is fully recorded in the proceedings of the Association of Official Agricultural Chemists, as published in their Journal, in the Methods Committee reports of the American Association of Cereal Chemists, as published in Cereal Chemistry, in committee reports of the American Dairy Science Association, published in the Journal of Dairy Science, and the various committee reports of the American Public Health Association, published in the American Journal of Public Health.

Dairy Chemistry. Whittier and Benton[1] showed that acid formation is a direct function of the time and temperature of heating, and that lactose is the principal source of the acid produced by heating milk. The effect of pasteurization at 62.5° on pure cultures of organisms found in milk was studied by Brannon and Prucha.[2] Only two of 47 nonspore-forming organisms survived pasteurization. Three colon organisms did not survive. No spore-formers were entirely eliminated by pasteurization. Cordes and Hammer[3] found that most of the pink yeasts common in milk and cream belong to a common type, *Torula glutinis*. The pH of the milk, exposed area, and time of exposure influence the

[1] Whittier and Benton, *J. Dairy Sci.*, **10:** 126 (1927).
[2] Brannon and Prucha, *J. Dairy Sci.*, **10:** 263 (1927).
[3] Cordes and Hammer, *J. Dairy Sci.*, **10:** 210 (1927).

amount of zinc dissolved from zinc containers according to Burke, Woodson and Heller.[4] Feeding tests with rats and swine indicated no deleterious effect. Bell, Peter and Johnson [5] obtained crude milk sugar from sweet whey by neutralizing with 5% sodium hydroxide to pH 7.3, separating, forewarming to 60°, condensing to 32° Bé. at 50°, cooling to 25°, and holding 42 hours at 40° with seeding. The lactose was recovered by centrifuging. By spray- or drum- drying the centrifugate, a soluble powder was obtained in which the casein and lactalbumin were in the ratio of 1 : 2. Greenbank, Steinbarger, Deysher and Holm,[6] in studying the effect of heat treatment of skimmed milk upon the baking quality of the evap- orated and dried products, found that there is a definite correla- tion between the viscosity of a 40% solution of a dry skimmed milk and its baking quality. In general, it was found that a powder giving a 40% solution of high viscosity yielded a better loaf than one producing a low viscosity at that concentration. Hartmann [7] studied the mashing process with regard to the temperature and time required for obtaining a suitable extraction of the malt- flour mixture used in the manufacture of malted milk. Processing an ice cream mix increased its viscosity, decreased the stability of the ice cream, increased the smoothness, and aided in the control of the freezing process, according to studies reported by Reid and Moseley.[8] Turnbow and Milner [9] studied the rôle of gelatin in ice cream and concluded that it is the most important ingredient in obtaining viscosity. Marquardt [10] showed that the quality of soft cheese varieties can be improved by homogenization and high pasteurizing temperatures of the milk or cream. Waterman [11] developed an interesting method for the determination of casein in milk by precipitating the casein with acid of a given concentra- tion containing a definite adjusted concentration of one of its alkali salts to form a buffer mixture of rather high concentration. The use of a fixed volume of such reagent gives a filtrate very near the iso-electric point. The Babcock and Gerber methods for determining fat in cream were found equally satisfactory for practical purposes by Dahlberg, Holm and Troy.[12] Newlander and

[4] Burke, Woodson and Heller, *J. Dairy Sci.*, **11**: 79 (1928).
[5] Bell, Peter and Johnson, *J. Dairy Sci.*, **11**: 163 (1928).
[6] Greenbank, Steinbarger, Deysher and Holm, *J. Dairy Sci.*, **10**: 335 (1927).
[7] Hartmann, *J. Assoc. Official Agr. Chem.*, **10**: 311 (1927).
[8] Reid and Moseley, *Mo. Agr. Expt. Sta., Res. Bull.* **91** (1926). 25 p.
[9] Turnbow and Milner, *J. Dairy Sci.*, **10**: 202 (1927).
[10] Marquardt, *J. Dairy Sci.*, **10**: 309 (1927).
[11] Waterman. *J. Assoc. Official Agr. Chem.*, **10**: 259 (1927).
[12] Dahlberg, Holm and Troy, N.Y. Agr. Expt. Sta., Tech. Bull., **122**: 13-32 (1926).

Ellenberger [13] found the wedge method of sampling butter for moisture analysis more accurate than the average trier. McRoberts and Remington [14] modified the Ferris method for gelatin so as to render it more accurate and better adapted for inspection analyses of ice cream.

Cereal Chemistry. Vogel and Bailey [15] studied durum wheats and found that durum wheat flour contains a higher average per cent of protein than average vulgare or common wheat flour, but that the proportion of glutenin to total protein is the same for both classes. The viscosity of leached and acidulated suspensions was lower, which served to distinguish the two types of flour. Studies on chemical and physical tests for determining the quality of gluten in wheat and flour by Coleman, Dixon and Fellows [16] showed that crude protein determination either on the wheat or flour milled from the wheat is the best single factor test, and that of the newer viscosity tests for determining baking strength, the single concentration test is the only satisfactory one. Coleman and Rothgeb [17] studied the physical characteristics and chemical composition of heat-damaged and header-damaged wheat of different varieties, the effect of the damage on yield and composition of flour, and the character of the resulting loaf. Barackman and Bailey [18] found that 0.2 and 0.4% of calcium acid phosphate increased the rate of carbon dioxide production, and did not appreciably affect the rate of loss of gas from the dough. A further study of the doughs in baking was reported by Grewe and Bailey,[19] who found that the increase in hydrogen ion concentration in dough fermentation improved the bread primarily because of the accelerated activity of the enzymes, particularly diastase, rather than by improvement in the physical properties of the dough. Grewe and Bailey [20] also studied the concentration of glutenin and other proteins in various types of wheat flour. No significant variation was detected in the ratio of glutenin to crude protein and of glutenin to the sum of glutenin and gliadin. Harding [21] described a new edible cellulose prepared from rice hulls by cooking with soda and subsequent hydration treatment, which is used in the manufacture of a break-

[13] Newlander and Ellenberger, Vt. Agr. Expt. Sta., Bull. 263 (1927).
[14] McRoberts and Remington, *J. Assoc. Official Agr. Chem.*, **10**: 315 (1927).
[15] Vogel and Bailey, *Cereal Chem.*, **4**: 136 (1927).
[16] Coleman, Dixon and Fellows, *J. Agr. Research*, **34**: 241 (1927).
[17] Coleman and Rothgeb, U.S. Dept. Agr., Tech. Bull., 6 (1927). 31 p.
[18] Barackman and Bailey, *Cereal Chem.*, **4**: 400 (1927).
[19] Grewe and Bailey, *Cereal Chem.*, **4**: 261 (1927).
[20] Grewe and Bailey, *Cereal Chem.*, **4**: 230 (1927).
[21] Harding, *Ind. Eng. Chem.*, **20**: 310 (1928).

fast food. Bracken and Bailey [22] found no deterioration in either Kanred or Turkey Red types of wheat as a result of delayed harvesting. New food products [23, 24] made from cereal germs, in which the starch is gelatinized and saccharified, are described. Cairus and Bailey [25] used eight chemical methods in studying the proteoclastic activity of flour. Foreman's titration method [26] was found to be rapid, but less satisfactory than the Sörensen formol titration method.[27] Determination of amino nitrogen by the Van Slyke method [28] was useful but more laborious than the Sörensen method. Blish, Abbott and Platenius [29] developed a new and simpler method for the estimation of glutenin in wheat flour which is referred to as the "barium hydroxide method," and depends on the solubility of glutenin in barium hydroxide and the insolubility of the barium "salt" of glutenin in methyl alcohol.

Fruit Chemistry. Chace and Church [30] continued their studies on the effect of ethylene on the composition and color of fruits and showed that this treatment does not appreciably alter the composition of citrus fruits, but does accelerate the coloring. Ethylene hastens coloring of persimmons, destroys their astringency, and produces softening. "Fruit Jellies" [31] and "Fruit Jellies, IV, The Rôle of Salts," [32] two bulletins by Myers and Baker, are a continuation of the fundamental studies in jelly making begun at the Delaware Agricultural Experiment Station several years ago by Tarr. In these bulletins are discussed the effect on jelly formation of variations in hydrogen ion concentration, salt concentration with total acidity constant, and also with hydrogen ion concentration constant. The buffer action of fruit juices is largely due to the presence of salts in the juices. Rooker [33] discusses the following new uses of pectin: (1) As an emulsifying agent; (2) as a glue or mucilage; (3) in confections; (4) in meringue powders; (5) crushed fruits for soda fountains; (6) as a blood agglutinant, and (7) "candy doctors." Myers and Baker in further studies on fruit jellies involving the rôle of pectin [34] point out that jelly

22 Bracken and Bailey, *Cereal Chem.*, **5**: 128 (1928).
23 Cregor, U.S.P. 1640182 (Aug. 23, 1927).
24 Hoffman U.S.P. 1640193 (Aug. 23, 1927).
25 Cairus and Bailey, *Cereal Chem.*, **5**: 79 (1928).
26 Foreman, *Biochem. J.*, **14**: 451 (1920).
27 Sörensen, *Biochem. Z.*, **7**: 45 (1908).
28 Van Slyke, *J. Biol. Chem.*, **9**: 185 (1911).
29 Blish, Abbott and Platenius, *Cereal Chem.*, **4**: 129 (1927).
30 Chace and Church, *Ind. Eng. Chem.*, **19**: 1135 (1927).
31 Myers and Baker, Del. Agr. Expt. Sta. Bull., **141**: 14-19 (1925).
32 Myers and Baker, Del. Agr. Expt. Sta., Bull., **144**: 3-35 (1926).
33 Rooker, *Fruit Products J. and Am. Vinegar Ind.*, 7, no. 1: 11 (1927).
34 Myers and Baker Del. Agr. Expt. Sta., Bull., **149** (1927). 46 p.

strength is a function of the viscosity of the pectin solution from which the jelly is made. Lathrop and Walde [35] studied the chemical composition of the Japanese quince and its uses as a fruit. A further study by the same authors [36] showed conclusively that no chemical change occurs in the composition of grape juice due to freezing storage other than the removal of 50% of the cream of tartar, and that grape jelly prepared from such stored juice is of a superior color and flavor. Culpepper and Caldwell [37] studied the relation of atmospheric humidity to the deterioration of evaporated apples in storage. Such apples stored at relative humidities of 18% or less retained their original color, odor and flavor. The rate of deterioration was more rapid in those varieties with high acid and low sugar content. A number of patents have been issued relating to fruits and fruit products. Citrus or other fruits are preserved by treatment with a mixture of paraffin and kerosene. [38] Apples or other fruit are preserved by immersing for 1 to 5 minutes in a sugar solution of boiling point (102-115°) to replace air in the fruit with sugar solution. [39] Citrus fruit is preserved with mixtures of paraffin and a volatile solvent such as gasoline and the paraffin emulsified with resinous soap, gum acacia and water. [40] The preparation of oranges, lemons and other fruit for market by washing with hot water, followed by a treatment in a bath containing water and an antiseptic such as borax and boric acid and maintained thereafter at a temperature of about 2° is described. [41] The preservation of berries and other fruits by subjecting them to the action of a concentrated sugar solution under pressure without cooking to replace part of the natural juice with sugar solution has been developed. [42] A jelly patent covers the drying of a mixture of sugar granules and pectin-containing substances and citric or other "fruit acid." [43] Glacé fruit is pre- pared by blanching followed by a short immersion in cold sirup, then cooking in the sirup *in vacuo* and saturating with the sirup and allowing to come to equilibrium. [44] Pectin is extracted by treat- ing apple pomace or other pectin-containing solution with dilute solutions of salts such as ammonium tartrate, which render soluble

[35] Lathrop and Walde, *Fruit Products J. and Am. Vinegar Ind.*, **7**, no. 4: 14 (1927).
[36] Lathrop and Walde, *Fruit Products J. and Am. Vinegar Ind.*, **7**, no. 5: 26 (1928).
[37] Culpepper and Caldwell, *J. Agr. Research*, **35**: 889 (1927).
[38] Brogden, U.S.P. 1628945 (May 17, 1927).
[39] Crawford, U.S.P. 1631017 (May 31, 1928).
[40] McDill, U.S.P. 1630129 (May 24, 1927).
[41] Barger, Hawkins and Blatz, U.S.P. 1632579 (June 14, 1927).
[42] McLaughlin, U.S.P. 1634295 (July 5, 1927).
[43] Leo, U.S.P. 1629716 (May 24, 1927).
[44] Jacobs, U.S.P. 1631487 (June 7, 1927).

all the pectin present.[45] The spoilage of fruits is checked by means of a solution of borax and boric acid according to a recent patent.[46] Fruit juices are concentrated by freezing and centrifuging the juices, then heating to a temperature below the boiling point, filtering to remove pectin and other undesirable substances, cooling to just above the freezing point and refiltering.[47] A jellyforming composition is described [48] as being obtained from fruits by extraction of the pectin with a fruit acid, such as citric or tartaric, to which solution sugar is added and the whole then dried by atomization. Apple juice [49] is prepared by the treatment of apple pomace with malt or other diastasic material at 60° to break down the starch cells; the entire material is then pressed and the juice filtered.

Vegetable Chemistry. The factors determining quality in sweetcorn were studied by Culpepper and Magoon,[50] who found that the most characteristic difference in composition is in the content of water-soluble polysaccharides. These constituents are relatively high in the sweetcorns and the waxy maize, but rather low in the flint, dent and flour types. The rate and type of fermentation of commercial sauerkraut was studied by Parmele, Fred, Peterson, McConkie and Vaughn.[51] They found the rate of acid production to be largely dependent on the temperature. Titratable acidity was found a better measure of the fermentation than pH determinations. The fermentation of cabbage is carried on by two distinctly different types of lactic acid-producing bacteria. Peterson, Parmele and Fred,[52] in studying the factors influencing the composition of cabbage and their relation to the quality of sauerkraut, found that cabbage grown on upland soil has less nitrogen and more sugar than that grown on marsh soil, and that the sauerkraut prepared from the former is superior. They also found that storage at high temperature or freezing is deleterious to sauerkraut. Lanman and Minton [53] found an improvement in the texture and flavor of vegetables by the addition of pure sodium chloride to the water before cooking and that the color is not noticeably changed when the sodium chloride is added at various times during

[45] Nanji, U.S.P. 1634879 (July 5, 1927).
[46] Cramer and Connell, U.S.P. 1635461 (July 12, 1927).
[47] Zorn, U.S.P. 1636890 (July 26, 1927).
[48] Leo, U.S.P. 1655398 (Jan. 3, 1928.
[49] Darling, U.S.P. 1659086 (Feb. 14, 1928).
[50] Culpepper and Magoon, *J. Agr. Research,* **34**: 413 (1927).
[51] Parmele, Fred, Peterson, McConkie and Vaughn, *J. Agr. Research,* **35**: 1021 (1927).
[52] Peterson, Parmele and Fred, *Soil Science,* **24**: 299 (1927).
[53] Lanman and Minton, Ohio Agr. Expt. Sta., Bull., **406**: 1-17 (1927).

the cooking operation. Werkman and Weaver [54] studied the "sulfur-stinker" spoilage of canned corn and ascribed it to a thermophilic, sporulating, heat-resistant anaërobe, for which the name *Clostridium nigri, cans* is proposed. Munger and Peterson [55] determined the manganese content of 10 vegetables and the loss of manganese by various methods of cooking. Steaming proved most efficient for preserving the manganese content and boiling in an excess of water the least. Spinach, string beans and beets have a high manganese content. Ford and Osborne [56] showed that waterless processing of vegetables in a vacuum results in an improved flavor and quality in canned foods.

Miscellaneous. Hepburn and Katz [57] reported data on the composition of the egg of the goose and the duck and the constants of the fat of the abdominal adipose tissue of both species. Weaver [58] used the formation of hydrogen sulfide by hydrogen sulfide-producing organisms as the basis of a test for incipient putrefaction of meats. The time required to blacken lead acetate paper in an anaërobic jar under vacuum at 37° C. is significant. Wilson, Turner and Sale [59] studied bottled cocoa beverages with particular reference to the use of hydrogen peroxide in such beverages, its persistence, relation to bacteria and yeasts, as well as methods for its detection. They found that the use of 1 to 5 cc. of hydrogen peroxide in cocoa-milk beverages merely retards the growth of yeasts and bacteria. Pederson and Breed [60] studied the preservative action in catsup of salt, sugar, benzoate and acid. Thirty-two bacterial and two yeast cultures (isolated from spoiled tomato products) were inoculated into 16 commercial brands of catsup. One % acid, 5% salt, and 0.2% benzoate was required to inhibit growth of the organisms used. Sugar was found ineffective. Victoria Carlsson [61] studied food changes in an ice refrigerator and an electrically controlled refrigerator. The results showed less bacterial increase and more efficient preservation in the electrically controlled refrigerator, probably because of lower temperature and lower humidity. Iszard [62] studied the value of lactic acid in the preservation of mayonnaise dressing and other products. She

[54] Werkman and Weaver, *Iowa State Coll. J. Sci.*, **2**: 57 (1927).
[55] Munger and Peterson, *J. Home Econ.*, **20**: 194 (1928).
[56] Ford and Osborne, *Glass Container*, **7**, no. 5: 5 (1928).
[57] Hepburn and Katz, *J. Franklin Inst.*, **203**: 835 (1927).
[58] Weaver, Mich. Agr. Expt. Sta., Tech. Bull. **79**: 1-28 (1927).
[59] Wilson, Turner and Sale, *Am. Food J.*, **22**: 244, 347 (1927).
[60] Pederson and Breed, N. Y. Agr. Expt. Sta., Bull. **538**: 3-15 (1926).
[61] Carlsson, *Teachers' Coll. Records*, **28**: 7.
[62] Iszard, *Glass Container*, 6, no. 4: 16 (1927).

found that lactic acid (1.75%) was the least amount necessary to prevent deterioration over a five months' period. Greenleaf [63] describes a new method for the estimation of milk-fat in milk-chocolate by means of a modified xylene number. A recent patent [64] covers the manufacture of food dressings by using a solution of pectin to emulsify vegetable oils or fats. A new preservative (methyl *p*-hydroxybenzoate) for use in preserving foods is described in a recent patent.[65] Sale and Wilson [66] describe the preparation of a concentrated maple flavoring by adjustment of maple sirup to a density of 28° Bé., heating to 80° and concentrating after precipitating the sugars with barium hydroxide.

[63] Greenleaf, *J. Assoc. Official Agr. Chem.*, **10**: 396 (1927).
[64] Douglas and Lorsch, U.S.P. 1625641 (Apr. 19, 1927).
[65] Sabalitschka, U.S.P. 1627342 (May 3, 1927).
[66] Sale and Wilson, U.S.P. 1642789 (Sept. 20, 1927).

Chapter XXVII.

Nitrogen Fixation.

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The nitrogen fixation industry in the United States has under- gone a conservative expansion during the past year, the plants now functioning having a combined capacity of roughly 35,000 tons of fixed nitrogen annually. The total output is in the form of synthetic ammonia, although cyanamide is manufactured in quantity at Niagara Falls, Canada. This synthetic ammonia finds its principal outlets in the refrigeration industry, in the manufac- ture of nitric acid and in the production of nitrogen oxides for chamber sulfuric acid plants. For these purposes the anhydrous ammonia of high purity which is obtained by direct synthesis is preferred to the by-product ammonia from the coke ovens, and at present prices ammonia is a cheaper source of nitrogen oxides and nitric acid than is Chile nitrate.[1] Up to the present, however, domestic synthetic ammonia has not found its way into fertilizer products. Although it is reported that the two largest producers of synthetic ammonia in this country expect to enter the fertilizer market in the near future, McBride[2] points out that the present costs of producing synthetic ammonia in this country and con- verting it into fertilizer products do not permit competition with either Chile nitrate or synthetic nitrogen imported from Germany. It is evident that a considerable advance in domestic technology will be required before the United States can become independent of foreign sources of nitrogen compounds.

A welcome addition to the literature of nitrogen fixation is a monograph by Ernst,[3] which emphasizes particularly the economic and engineering aspects of the industry and includes statistical data of great value.

[1] Killefer, *Ind. Eng. Chem.*, **19**: 1077 (1927).
[2] McBride, *Chem. Met. Eng.*, **35**: 52 (1928).
[3] Ernst, "Fixation of Atmospheric Nitrogen." New York, Van Nostrand Co., **1928**.

Direct Synthetic Ammonia Process. A number of papers of technical or economic interest have appeared during the past year. Tour [1] has made a detailed study of synthetic ammonia costs in America and Morris [5] has discussed possible future outlets for ammonia. Quinn [6] gives a brief account of the trend of the industry in 1927. The achievement of the Commercial Solvents Corporation in successfully producing synthetic ammonia and methanol from the waste gases of corn fermentation is described by Woodruff.[7] Ernst and Edwards [8] present detailed designs for a plant to produce ammonium sulfate by the sulfuric acid absorption method. As a step in the technical development of the urea synthesis from ammonia and carbon dioxide, Clark and Hetherington [9] have obtained an accurate value of the heat of formation of ammonium carbamate. Vanick and collaborators [10] report the results of a comprehensive study of the deterioration of alloy steels in the synthesis of ammonia. The numerous patents granted for new catalysts, equipment and methods of operation indicate a continued intensive study of the technical features of the process.

The excellent work in the Bureau of Chemistry and Soils on the properties of gases at high pressures has been continued. In two papers Bartlett and his collaborators [11] give complete data for the compressibility isotherms of hydrogen, nitrogen and mixtures of the two at temperatures from 0 to 400° and pressures to 1000 atmospheres. From these results on mixtures Merz and Whittaker [12] have calculated the free energy and fugacity of each constituent and show that at high pressures these mixtures can not be regarded as perfect solutions. Lurie and Gillespie [13] have investigated the deviations from Dalton's law of partial pressures in mixtures of ammonia and nitrogen and Keyes and Burks [14] derive an equation of state for binary mixtures of nitrogen and methane. Everett [15] has calculated the entropy of nitrogen and other gases over a wide range of temperature.

[4] Tour, *Chem. Met. Eng.,* **35**: 89, 162 (1928).
[5] Morris, *Ind. Eng. Chem.,* **19**: 912 (1927).
[6] Quinn, *Chem. Met. Eng.,* **35**: 48 (1928).
[7] Woodruff, *Ind. Eng. Chem.,* **19**: 1147 (1927).
[8] Ernst and Edwards, *Ind. Eng. Chem.,* **19**: 768 (1927).
[9] Clark and Hetherington, *J. Am. Chem. Soc.,* **49**: 1909 (1927).
[10] Vanick, *Trans. Am. Soc. Steel Treating,* **12**: 169 (1927); Thompson, *Iron Age,* **120**: 1518 (1927); Vanick, de Sveshnikoff and Thompson, Bur. of Standards, *Tech. Paper* No. 361 (1927).
[11] Bartlett, *J. Am. Chem. Soc.,* **49**: 1955 (1927); Bartlett, Cupples and Tremearne, *ibid.,* **50**: 1275 (1928).
[12] Merz and Whittaker. *J. Am. Chem. Soc.,* **50**: 1522 (1928).
[13] Lurie and Gillespie, *J. Am. Chem. Soc.,* **49**: 1146 (1927).
[14] Keyes and Burks, *J. Am. Chem. Soc.,* **50**: 1100 (1928).
[15] Everett, *Mech. Eng.,* **48**: 1329 (1926).

Interesting work has been reported during the year on the mechanism of ammonia synthesis. Lewis [16] finds that ammonia is formed from atomic hydrogen and active nitrogen but not from atomic hydrogen and ordinary nitrogen nor from active nitrogen and molecular hydrogen. Using a flow system, Lind and Bard-well [17] show that ammonia is formed from hydrogen and nitrogen under the influence of α-radiation, but at the rate of only 0.2-0.3 molecule per ion pair. Wendt and Snyder [18] have found that a steady value of 4.1% ammonia may be obtained from a $3:1$ mixture of hydrogen and nitrogen in a corona discharge at ordinary temperature and pressure. Dew and Taylor [19] have measured the adsorption and heat of adsorption of ammonia gas on metallic catalysts. Keyes [20] has discussed chemical equilibrium in imperfect gases, with special reference to ammonia synthesis.

Several papers have appeared on ammonia decomposition. Burk [21] has studied the action of a molybdenum wire as catalyst and Kunsman [22] finds that the apparent heat of activation for ammonia decomposition on various promoted and poisoned iron catalysts is approximately the same, although the activities varied eighteenfold. Much attention has been given to the photochemical decomposition of ammonia. Kassel and Noyes,[23] using relatively short wave lengths, find a higher quantum efficiency than previous workers. The photosensitized decomposition in presence of mercury vapor has been studied by Dickinson and Mitchell [24] and by Bates and Taylor.[25] Studies on the thermal and photochemical decomposition of hydrazine [26] are closely related to the work on ammonia.

Hydrogen and Nitrogen. General discussions of the production and uses of hydrogen are given by Stuart [27] and by Wilson.[28] There are many indications of the increasing interest in coke-oven gas and natural gas as sources of hydrogen and a

[16] Lewis, *J. Am. Chem. Soc.*, **50**: 27 (1928).
[17] Lind and Bardwell, *J. Am. Chem. Soc.*, **50**: 745 (1928).
[18] Wendt and Snyder, *J. Am. Chem. Soc.*, **50**: 1288 (1928).
[19] Dew and Taylor, *J. Phys. Chem.*, **31**: 277 (1927).
[20] Keyes, *J. Am. Chem. Soc.*, **49**: 1393 (1927).
[21] Burk, *Proc. Nat. Acad. Sci.*, **13**: 67 (1927).
[22] Kunsman, *Science*, **65**: 527 (1927).
[23] Kassel and Noyes, *J. Am. Chem. Soc.*, **49**: 2495 (1927).
[24] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**: 692 (1926); Mitchell and Dickinson, *J. Am. Chem. Soc.*, **49**: 1478 (1927); Mitchell, *ibid.*, **49**: 2699 (1927).
[25] Bates and Taylor, *J. Am. Chem. Soc.*, **49**: 2438 (1927); Taylor, *Ind. Eng. Chem.*, **20**: 439 (1928).
[26] Elgin, Askey and Taylor, Paper read at St. Louis Meeting of the American Chemical Society, April 16-19, 1928.
[27] Stuart, *Ind. Eng. Chem.*, **19**: 1321 (1927).
[28] Wilson, *Gen. Elec. Rev.*, **30**: 544 (1927); **31**: 197 (1928).

number of patents have been granted covering the electrolytic generation of hydrogen at high pressure. Nevertheless in this country, as in Germany, water-gas continues to represent the principal source of hydrogen.

Although some of the industries concerned are carrying on extensive research programs on hydrogen production, there have been no American published contributions on this subject during the past year. Information of great value has been obtained, however, on many reactions of hydrogen which are of interest in connection with the removal of carbon monoxide and other catalyst poisons. Smith [29] and Francis [30] have calculated from available thermodynamic data the equilibrium conditions in the formation of hydrocarbons and alcohols from water-gas. Smith, Davis and Reynolds [31] have investigated the action of a variety of catalytic agents in the synthesis of higher hydrocarbons from water-gas at atmospheric pressure and Hightower and White [32] have studied the synthesis of methane from water-gas. Lewis and Frolich [33] have carried out similar studies on the formation of methanol and higher alcohols at high pressures. Huff and Holtz [34] have investigated the carbon-sulfur complex which they find is involved in the formation of carbon disulfide in gas making. Thiele and Haslam [35] have studied the mechanism of the steam-carbon reactions, and Davis and Reynolds [36] have examined the effect of the physical characteristics of coke on its reactivity with air, steam and carbon dioxide.

A large number of patents has been issued on the production of nitrogen, especially from liquid air. Dodge and his collaborators [37] have reinvestigated the vapor pressure of oxygen and nitrogen and the coexisting liquid and vapor phases of their solutions, with results that differ from those of earlier workers.

Arc Process. Although the arc process is now being abandoned even in Norway, where conditions were formerly considered most favorable to this process, much theoretical and practical interest attaches to the question of the exact thermal equilibrium in the formation of nitric oxide and the possible influence of elec-

[29] Smith, *Ind. Eng. Chem.*, **19**: 801 (1927).
[30] Francis, *Ind. Eng. Chem.*, **20**: 277, 283 (1928).
[31] Smith, Davis and Reynolds, *Ind. Eng. Chem.*, **20**: 462 (1928).
[32] Hightower and White, *Ind. Eng. Chem.*, **20**: 10 (1928).
[33] Lewis and Frolich, *Ind. Eng. Chem.*, **20**: 285, 354 (1928).
[34] Huff and Holtz, *Ind. Eng. Chem.*, **19**: 1268 (1927).
[35] Thiele and Haslam, *Ind. Eng. Chem.*, **19**: 882 (1927).
[36] Davis and Reynolds, *Ind. Eng. Chem.*, **20**: 617 (1928).
[37] Dodge and Dunbar, *J. Am. Chem. Soc.*, **49**: 591 (1927); Dodge and Davis, *ibid.*, **49**: 610 (1927).

trical or other forms of energy on this equilibrium. Colin and Tartar [38] have continued their work on the formation of nitric oxide in the high tension arc at different pressures. Krase [39] has employed recently published data to recalculate the free energies of formation of the nitrogen oxides and nitric acid. These calculations are of interest in connection with the claims of various European investigators that nitric oxide in excess of the ordinary thermal equilibrium is obtained when compressed mixtures of carbon monoxide and air are heated to a high temperature by explosion.

Cyanamide Process. Although no nitrogen is fixed in this country by the cyanamide process, the American Cyanamide Company at Niagara Falls, Canada, employs the process on a large scale. Most of the product is used in mixed fertilizers, but much of it is converted to other products, such as ammonia, hydrocyanic acid and various cyanides. An interesting recent development [40] consists in the treatment of hydrocyanic acid with acetaldehyde to form acetaldehydecyanohydrin, which is then acted upon with ethanol in presence of hydrochloric acid and a small amount of water, to form ammonia and ethyl lactate. Since the value of the latter lies in its use as a lacquer solvent, it is evident that the amount of ammonia which could be produced by this process is distinctly limited.

Ammonia Oxidation. The replacement of Chilean nitrate by ammonia as a source of nitric acid has developed rapidly during the past year and some excellent work on the oxidation process has been reported. Parsons [41] discusses the technical and economic aspects of the industry and Killefer [42] describes the process as a source of nitrogen oxides for chamber sulfuric acid plants. Taylor [43] devotes particular attention to the mechanism of the reactions involved in the absorption of the nitrogen oxides. His conclusions differ considerably from those reached in the recently reported investigations conducted at Rjukan, Norway, in 1918-1925. [44]

Numerous patents have been granted which aim to increase the efficiency of absorption by refrigeration or by oxidizing the ammonia with oxygen or air enriched with oxygen. If pure oxygen

[38] Colin and Tartar, *J. Phys. Chem.*, **31**: 1539 (1927).
[39] Krase, *J. Phys. Chem.*, **32**: 463 (1928).
[40] Matheson and Blaikie, Can. P. 263186 (Aug. 3, 1926).
[41] Parsons, *Ind. Eng. Chem.*, **19**: 789 (1927).
[42] Killefer, *Ind Eng. Chem.*, **19**: 1153 (1927).
[43] Taylor, *Ind. Eng. Chem* **19**: 1250 (1927).
[44] Homesland, *Tids. Kemi Bergvesen*, **6**: 107 (1927).

could be used without explosion or deleterious action on the cata-lyst, the product could be obtained in the form of liquid nitrogen tetroxide, which Pinck [45] has shown can be successfully substituted for nitric acid in organic nitrations and for which numerous other uses could presumably be found. Morris [46] has investigated the practicability of producing a two-constituent fertilizer by the direct absorption of the nitrogen oxides in an aqueous suspension of phosphate rock.

Although high-chromium steels have solved the serious corrosion problem in the absorption towers, intensive studies in this country and abroad [47] indicate that the tower system may practically be dis-pensed with entirely if the oxidation and absorption are carried out at about 100 lbs. pressure. There are said to be no attendant dis-advantages of a serious nature.

Miscellaneous. Burk [48] has employed thermodynamic data as an aid in the study of nitrogen fixation by living forms. Halver-sen [49] finds evidence that ammonia may be the first product of the nitrogen metabolism of nitrogen-fixing bacteria. In attempts to achieve photosynthesis in presence of ammonia, Burk [50] found that no biochemical nitrogen compounds were synthesized, but in pres-ence of ferric chloride ammonia was oxidized to nitrates and to nitrites and nitrates in presence of zinc oxide or mercuric oxide.

[45] Pinck, *J. Am. Chem. Soc.*, **49**: 2536 (1927).
[46] Morris, *Ind. Eng. Chem.*, **19**: 1143 (1927).
[47] Compare Fauser, Address at International Nitrogen Conference on the Adriatic, May, 1928.
[48] Burk, *J. Gen. Physiol.*, **10**: 559 (1927).
[49] Halversen, *Iowa State Coll. J. Sci.*, **1**: 395 (1927).
[50] Burk, *J. Phys. Chem.*, **31**: 1338 (1927).

Chapter XXVIII.

Water and Sewage.

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Progress in water chemistry has been marked by no particular trend during the past year but reports of sewage research have in dicated that the subjects of sludge digestion, sewage chlorination and the aeration of sewage and polluted water are of greatest in terest. The year has been marked by the appearance of several excellent books, including Buswell's "The Chemistry of Water and Sewage Treatment"; Martin's "The Activated Sludge Pro cess," which, although written by an English author, is a fairly up-to-date review of American work; Powell's "Boiler Feed Water Purification"; Jordan's "The Newer Knowledge of Bacteriology"; and several others. Much information of value in water and sewage work appears in annual reports of experiment stations, which have a limited circulation.

Water Purification and Softening

Streeter[1] has reported the results of exhaustive studies of the bacterial efficiency of 10 filter plants on the Ohio River and 7 in other parts of the country. He concluded that the *Bact. coli* index (per 100 cc.) of the raw water could not exceed 5,000 in order to produce a filtered, chlorinated water with an index of 1.0 or less, the U. S. Treasury Standard. If filtered but not chlorinated, the index of the raw water should not exceed 60 in order to meet the standard.

Chlorination. Chlorination thus allows the use of a more heavily polluted raw water. Pre-chlorination has been used at Quincy, Ill.,[2] Toronto, Ont.,[3] Raleigh, N. C.[4] Sandusky, Ohio,[5]

[1] Streeter, U.S. Public Health Service, Bull. 172 (1927). 423 p.
[2] Gelston, *Eng. News-Record*, 100: 407 (1928).
[3] Howard, *J. Am. Water Works Assoc.*, 19: 546 (1928).
[4] J. N. Car. Water Works Assoc., 5: 101 (1927).
[5] 6th Report, Ohio Water Works Conference, p. 237 (1927).

Dallas, Texas,[6] and various other places. This practice has been preferable to a single heavy dose of chlorine after filtration.

Chlorination of water produces highly objectionable tastes when minute amounts of phenol are present. These tastes were present in the Chicago[7] water supply in unprecedented amounts in the early part of 1928. In order to detect the minute quantity of phenols present in Lake Michigan water Baylis[8] has improved and modified Gibbs'[9] method, using the color reaction with 2,6-dibromoquinonechloroimide. Donaldson and Furman[10] reported that tastes in Toledo chlorinated water could be detected with 80 parts per billion phenol but only 20 parts per billion cresols.

Howard[3] has reported further concerning the practice of super- and de-chlorination used at Toronto for the purpose of eliminating these tastes. Approximately 12.5 lb. chlorine per million gallons is applied and after 1.25 hours contact the residual chlorine is removed by sulfur dioxide. It is claimed that this procedure removes tastes. Harrison[11] has used the same procedure successfully at Bay City, Michigan. On the contrary, McAmis did not have success with it at Greeneville, Tenn., and used Houston's ammonia-chlorine process.

Chlorphenol Tastes. It must be admitted that attempts of this sort to destroy or eliminate chlorphenol tastes are not uniformly successful. The most practical solution of the problem is the recovery of phenol from ammonia-still waste. Tisdale[12] has reported on the progress of recovery at a number of plants in Pennsylvania, Ohio and West Virginia. Studies have been made at Rochester, N. Y.,[13] of the feasibility of discharging ammonia-still waste into sewers. Crawford[14] has described the plant at Rensselaer, N. Y., in which phenol is extracted by benzol or light oil, followed by treatment with a solution of sodium hydroxide, the plant working on the counter-current principle. Recoveries of phenol of from 70 to 98% are claimed for this process. Jones[15] has described the same type of plant at Fairmont, W. Va., where very successful results have been obtained. Bundesen[16] has re-

[6] Bakke, *Water Works,* **66**: 109 (1927).
[7] *Eng. News-Record,* **100**: 115 (1928).
[8] Baylis, *J. Am. Water Works Assoc.,* **19**: 597 (1928).
[9] Gibbs, *Chem. Reviews,* **3**: 291 (1926).
[10] Donaldson and Furman, *Can. Eng.,* **53**: 203 (1927).
[11] Harrison, *J. Am. Water Works Assoc.,* **17**: 336 (1927).
[12] Tisdale, *Water Works,* **66**: 284 (1927).
[13] Caird, *J. Am. Water Works Assoc.,* **18**: 526 (1927).
[14] Crawford *Ind. Eng. Chem.,* **19**: 966 (1927).
[15] Jones, *Chem. Met. Eng.,* **35**: 215 (1928).
[16] Bundesen, *Water Works,* **67**: 240 (1928).

viewed present practice in phenol recovery and gives data con-
cerning the problem in the Calumet region at Chicago.

A standard test for determining chlorphenol tastes has been
adopted by a committee representing coke plant and public health
officials in Pennsylvania, Ohio and West Virginia.[17]

This problem of tastes and odors in water supplies has un-
doubtedly been one of the most important subjects before Ameri-
can water chemists during the past year.

Aeration and Filtration. In its broader aspects the practice
of water purification is fairly well standardized, but some of the
filter plants built during the past year have novel features of
design, and have reported operating results of interest. Aeration
of the filter effluent of the new 20 million gallon per day plant at
West Palm Beach, Fla.,[18] reduced CO_2 from 7.5 to 4.4 p.p.m.
Whipple and Chandler [19] report a reduction from 10.5 to 7.5 p.p.m.
at the Cambridge (Mass.) plant. Bugbee and Bean [20] report about
30% decrease at the Providence plant. Complaints of "red water"
and corrosion at Harrisburg, Pa.,[21] with an average CO_2 content
of 5 p.p.m., led to the use of lime for neutralization, with suc-
cessful results. Baylis [22] has contended for some time that the
difficulties of "aggressive CO_2," corrosion, and red water can be
minimized by addition of lime.

Results of aeration in Texas have been described by Mahlie,[23]
who claims that 127 tests at Fort Worth indicated that aeration
reduced the 37° agar count by 35.6%.

Reports from the iron-removal plant at Champaign, Ill.,[24] indi-
cate that chlorination was required in addition to aeration. A new
plant has been built at Albuquerque, New Mexico.[25]

Removal of color is discussed by Weston.[26]

Coagulation and clarification have been studied at a number
of plants. Alum syrup is to be manufactured at the new Wash-
ington, D. C., plant,[27] as at Baltimore, Sacramento and other places.
Sodium aluminate has been tried out at a number of places. It
was reported to be expensive and unsatisfactory at Akron and

[17] J. Am. Water Works Assoc., 19: 605 (1928).
[18] Eng. News-Record, 98: 1048 (1927).
[19] Whipple and Chandler, J. New England Water Works Assoc., 41: 218 (1927).
[20] Bugbee and Bean, J. New England Water Works Assoc., 41: 399 (1927).
[21] Gould, J. Am. Water Works Assoc., 19: 358 (1928).
[22] Baylis. Ind. Eng. Chem., 19: 777 (1927).
[23] Mahlie, J. Am. Water Works Assoc., 19: 693 (1928).
[24] Amsbary, J. Am. Water Works Assoc., 19: 522 (1928).
[25] Veatch, Eng. News-Record, 100: 845 (1928).
[26] Weston, J. Am. Water Works Assoc., 19: 416 (1928).
[27] Macqueen, J. Am. Water Works Assoc., 19: 483 (1928).

Portsmouth, Ohio,[28] but Powell[29] claims it has advantages over alum. It is reported to be superior to alum at Hinsdale, Illinois.[30]

Peterson and Bartow[31] report experiments on the effect of salts on the rate of formation of alum floc. Their results indicate that pH control is only one factor in the production of a floc and that variations in sulfate content are probably of more importance. With a fixed sulfate content the range of pH is quite wide for satisfactory flocculation (5.7 to 7.1 with 500 p.p.m. Na_2SO_4).

Water Softening. Water softening has been reviewed by Hoover.[32] The Columbus, Ohio, plant has used lime for many years. The normal carbonates present in the treated water pre- cipitate on the grains of the sand of the filters, in hot water lines and in small fittings. Re-carbonation with CO_2 seems to be the remedy for this difficulty. A large plant for this purpose is being built at St. Louis.[33] Hoover[34] recommends burning coal or water gas for CO_2 production for small plants as at Hinsdale[30] and Fostoria, Ohio,[35] and producer gas for large plants as at Columbus. An oil burner is used at the large new plant at Miami, Florida.[36]

Spaulding[37] reports that excellent bacterial results are obtained at the Springfield, Ill., plant by the use of 1500 lb. lime per mil- lion gallons. The excess lime method has been in use for some time at Youngstown, Ohio,[38] but it will probably be abandoned there because of the high temperature and excessive pollution of the raw water from the Mahoning River and an impounded supply developed.

Results of experiments on zeolite softening for a large central heating plant at Detroit have been reported by White.[39] Con- tinuous blow-down was advised to prevent undue concentration of alkali salts. Double treatment using the lime-soda process fol- lowed by zeolite treatment seems to be preferable to over-all zeolite softening. Recent practice in water softening for locomo- tives has been reviewed by Barr and Savidge.[40]

Water Analysis. New media for simpler and more accurate

[28] Gettrust and Sheehan, Ohio Conference on Water Purification, no. 6: 81 (1927).
[29] Powell, *Am. J. Public Health*, 17: 804 (1927).
[30] *Eng. News-Record*, 100: 616 (1928).
[31] Peterson and Bartow, *Ind. Eng. Chem.*, 20: 51 (1928).
[32] Hoover, *J. Am. Water Works Assoc.*, 17: 751 (1927).
[33] Graf, *Eng. News-Record*, 99: 643 (1927).
[34] Hoover, *Ind. Eng. Chem.*, 19: 784 (1927).
[35] Laboon, *J. Am. Water Works Assoc.*, 19: 503 (1927).
[36] Howson, *Water Works*, 66: 267 (1927).
[37] Spaulding *J. Am. Water Works Assoc.*, 18: 60 (1927).
[38] Dittoe, Ohio Conference on Water Purification, no. 6: 56 (1927).
[39] White, *J. Am. Water Works Assoc.*, 18: 219 (1927).
[40] Barr and Savidge, *J. Am. Water Works Assoc.*, 18: 728 (1927).

determination of *Bact. coli* have been reported during the past year. Jordan [41] collected results from fifteen laboratories in which brilliant green bile was compared with the standard completely-confirmed test for the coli-aerogenes group. It was found that 2% bile was better than 5% but direct implantation even into 2% gave low results. However, when the sample was first introduced into lactose broth, incubated 24 hours at 37° C. and then intro-duced into weak brilliant green bile, the inhibition was almost eliminated and the brilliant green bile results were 95% of the completely confirmed. This conclusion is in line with the previous results of Ruchhoft.[42] Lewis and Pittman [43] claim as a result of work on Texas waters that Koser's citrate test gives better cor-relation with the sanitary quality of water (fecal or non-fecal organisms) than the methyl red or Voges-Proskaner tests. Noble [44] is attempting to work out a complex solid medium containing agar, lactose, phosphates, potassium ferrocyanide, and ferric citrate for the direct enumeration of coli-aerogenes colonies.

Chemical analyses of river waters are still being made by the U. S. Geological Survey. Collins [45] has reported the results of analyses of many samples collected from the Colorado River at the Grand Canyon. These results are of considerable interest and value because of the great public interest in the advantages and disadvantages of Boulder Dam, particularly the danger of rapid silting and the questionable value of such hard water for a potable supply.

SEWAGE TREATMENT

Research. Sewage research during the past year has centered mainly on the oxygen requirements of sewage, the chlorination of sewage and effluents, and the digestion of sewage sludge.

An outstanding monograph on the biochemical oxygen demand determination was issued by Theriault.[46] This determination is of extreme importance in problems of sewage treatment and stream pollution, but it has required considerable research to demonstrate that the method could be made reliable and accurate. Theriault gives the details of manipulation, also data on the precision ob-

[41] Jordan, *J. Am. Water Works Assoc.*, **18**: 337 (1927).
[42] Ruchhoft *J. Am. Water Works Assoc.*, **16**: 778 (1926).
[43] Lewis and Pittman, *J. Am. Water Works Assoc.*, **19**: 78 (1928).
[44] Noble, *J. Am. Water Works Assoc.*, **19**: 182, 933 (1928).
[45] Collins, U.S. Geol. Survey, Water Supply Paper 596B (1927).
[46] Theriault, U.S. Public Health Service, Bull. 173 (1927).

tainable. He shows that the rate of demand for freshly polluted waters follows the logarithmic course of a first-order reaction during the first stage of decomposition and gives equations for determining the rate and magnitude of the demand. Mohlman, Edwards and Swope [47] conclude that the dilution method is pref erable to the nitrate method for biochemical oxygen demand determination, provided care is taken in analytical procedure and a standardized dilution water is used. Distilled water gave low results. Two stages were found in the biochemical oxygen demand of sewage, as shown by Theriault, but only one stage with starch waste. Data indicate that the secondary increase in biochemical oxygen demand is correlated with an increase in nitrate. Rates of biochemical oxygen demand change as a stream undergoes self purification. Studies of sewage and effluents in various stages of purification gave curves similar to those obtained on samples from the Illinois River.

The present status of the chlorination of sewage and effluents has been reviewed by Enslow.[48] Tiedemann [49] reported results of chlorination of Imhoff effluent at Huntington, New York. Re sidual chlorine of 0.2 p.p.m. by o-tolidine with contact periods of 5 minutes gave 99.8% reduction of $B.$ $coli.$ The chlorine pene trated the solids quite effectively. Chlorine demand varied from 6.5 p.p.m. in February to 12.0 or 13.0 p.p.m. in July and August. Mahlie [50] chlorinated trickling-filter effluent at Fort Worth, Texas. Approximately 3.5 p.p.m. greatly improved the effluent of the secondary sedimentation tanks by retarding septicization. Scott and Pool [51] chlorinated screened sewage at Bridgeport and re ported that 15 p.p.m. was required. Cohn [52] has made further study of chlorination at Schenectady. Application of 6.0 p.p.m. to the raw sewage reduced odors. Filter flies (*Psychoda alternata*) were not eliminated by application of 25 p.p.m. to the filter influent for 24 hours at two-week intervals. Biological films on filter stone were removed by this treatment. Odors have been prevented to some extent at Plainfield, N. J.,[53] by application of 12 p.p.m. chlorine after screening. At Haddonfield 20 p.p.m. was required to give residual chlorine and eliminate H_2S. It was claimed by

[47] Mohlman, Edwards and Swope, *Ind. Eng. Chem.,* **20:** 242 (1928).
[48] Enslow, *Water Works,* **66:** no. 12: 505 (1927).
[49] Tiedemann, *Eng. News-Record,* **98:** 944 (1927).
[50] Mahlie. *Public Works,* **58:** 264 (1927).
[51] Scott and Pool, *Eng. News-Record,* **99:** 1030 (1927).
[52] Cohn, *Eng. News-Record,* **99:** 229 (1927).
[53] Public Works, **59:** 163 (1928).

Hackmaster [54] that application of 3.32 p.p.m. chlorine to the crude sewage of Independence, Kansas, eliminated odors from the Imhoff tanks and trickling filters. Rudolfs and Zeller [55] reported that heavy doses of chlorine to the Plainfield, N. J., filter influent did not eliminate filter flies.

Sludge digestion has been studied at various sewage experiment stations, particularly the New Jersey Sewage Experiment Station, New Brunswick, under the direction of W. Rudolfs. The annual report for 1927 [55] gives interesting data on the digestion of sludge in two separate sludge digestion tanks at Plainfield. The sludge was heated to 68° F. and pH adjusted to 7.3 by addition of lime. Good digestion occurred in 40 days but the moisture content of the sludge as drawn was quite high, averaging 92.5%, and the amount of gas collected was quite low, because of leaks in the wooden cover of the tank. Seeding materials for starting new digestion tanks are of decreasing value as follows: ripe sludge, sludge or mud from polluted river bottoms, cow or horse manure.

The beneficial effect of lime on digestion was reported by Rudolfs in his 1926 Report. Fair and Carlson [56] used limestone for control and report that the time of digestion for uncontrolled sludge was 24 weeks, that of controlled sludge 8 weeks. Their results indicate that pH of 6.8 is probably the optimum for the first stage of digestion and 7.2 for the final stage. Fair and Carlson [57] also studied the effect of chlorine on sludge digestion and report that laboratory experiments indicated that Imhoff sludge from Schenectady which had been treated with 10 p.p.m. chlorine, leaving a residual of 1.5 p.p.m., digested slightly more rapidly than sludge from an adjacent tank which had not been chlorinated.

The source of the excessive acidity and CO_2 production during the first few weeks of uncontrolled sludge digestion has been of interest. Heukelekian [58] claims that cellulose decomposes quite rapidly and gives results of experiments on Plainfield sludge which indicate that from 80 to 95% of the initial cellulose disappeared in the first three weeks. Approximately 10% of the organic content of the fresh sludge was cellulose. Rudolfs [55] confirms and amplifies these conclusions in his 1928 Annual Report. On the other hand, Neave and Buswell [59] ran digestion experiments with

[54] Hackmaster, *Eng. News-Record*, **99**: 1031 (1927).
[55] Rudolfs and Zeller, Annual Rept., Sewage Expt. Sta., New Brunswick, N.J., 1927.
[56] Fair and Carlson, *Eng. News-Record*, **99**: 881 (1927).
[57] Fair and Carlson, *Eng. News-Record*, **99**: 103 (1927).
[58] Heukelekian, *Ind. Eng. Chem.*, **19**: 928 (1927).
[59] Neave and Buswell, *Ind. Eng. Chem.*, **19**: 1012 (1927).

Urbana (Ill.) sludge which showed practically no loss of cellulose in 9 weeks. They claim that grease and lime soaps decompose most rapidly and are responsible for the initial acid stage of sludge digestion. The initial content of grease in the sludge used was 35% of the organic matter, cellulose only 17%. Increasing gas production was found with increasing content of grease.

Heukelekian and Rudolfs [60] claim that nitrogen does not disappear during sludge digestion. Their experiments were carried out to 240 days at 24° C. There was an absolute reduction of carbon but an increase in the per cent of carbon in the volatile matter.

Hatfield, Symons and Mills [61] found very rapid digestion of Imhoff sludge at Decatur, Ill., where 50% of the sewage flow is waste from a starch plant, which is quite warm and concentrated, high in sulfates and starch. The gas contained up to 0.95% H_2S, increasing with the temperature of sewage, which varied from 20° to 40° C. throughout the year. Rudolfs and Zeller [62] studied the effect of sea water on sludge digestion and report that the retardation of gas production is slight with as much as 10 grams per liter of NaCl. Sulfates were almost completely decomposed, mainly to free sulfur. H_2S was found in increasing amounts with increase in sulfates but the maximum H_2S production was only 5.6% of the sulfur originally present as sulfates.

Rudolfs and Zeller,[63] and Fair and Carlson [64] have reported that activated sludge digests quite well when properly seeded, also that control of pH by lime (Rudolfs) and calcium carbonate (Fair) stimulated gas production. Fair and Carlson reported fairly high yields of gas from unseeded activated sludge. Rudolfs concluded that the amount of gas from activated sludge, either seeded or unseeded, was less than from an equal weight of organic matter in fresh sewage solids, and Imhoff [65] had also reached this conclusion several years earlier. The differences may have been on account of the high temperature of incubation, 37° C., used by Fair as compared with 20° C. used by Imhoff and Rudolfs.

Activated Sludge. Cramer and Wilson [66] have reported on the present status of operation of the Milwaukee activated sludge

[60] Heukelekian and Rudolfs, *Ind. Eng. Chem.*, **20**: 177 (1928).
[61] Hatfield, Symons and Mills, *Ind. Eng. Chem.*, **20**: 174 (1928).
[62] Rudolfs and Zeller, *Ind. Eng. Chem.*, **20**: 48 (1928).
[63] Rudolfs and Zeller, *Public Works*, **58**: 253 (1927).
[64] Fair and Carlson, *J. Boston Soc. Civil Eng.*, **14**: 487 (1927).
[65] Imhoff, *Eng. News-Record*, **94**: 936 (1925).
[66] Cramer and Wilson, *Public Works*, **59**: 20 (1928).

plant. It is now treating the capacity flow of sewage, 86 million gallons per day, from which 100 tons of dry fertilizer are produced. The cost of operation for pressing and drying sludge is reported to be slightly less than its net selling price. Sulfuric acid, alum, chlorinated copperas and ferric chloride are used for coagulation of sludge and are increasingly efficient in the order named. Chlorine is used for deodorizing the dryer discharge. Kadish [67] states that the sludge sells readily and averages 5.4% nitrogen and 3.1% phosphoric acid. Wilson and Cramer [68] consider the action of activated sludge to be physico-chemical and not dependent on bacterial action. They claim to have purified sewage in contact with activated sludge by aerating with a mixture of air and chlorine equal to 300 lb. chlorine per million gallons of sewage.

Mohlman and Palmer [69] describe experiments on coagulants for activated sludge, particularly the discovery of the value of ferric salts which had not been used previously. Ferric chloride was too expensive but a fairly cheap substitute, although not as effective, was found by chlorinating copperas, giving a mixture of ferric chloride and sulfate.

Activated sludge from the Indianapolis activated sludge plant is digested with settled sludge in large open pits. Calvert [70] claims that it dries to a non-odorous sludge of 85% moisture content which contains 4.5% nitrogen on the dry basis. It is in great demand locally for fertilizer.

Activated sludge plants are now in operation at many American cities, including Milwaukee, Indianapolis, Chicago, Houston, Waco (Texas), Tenafly (N.J.), Mamaroneck (N. Y.), Pasadena and Pomona (Cal.), Gastonia and Charlotte (N. C.) and at numerous smaller cities. The North Side activated sludge plant of the Sanitary District of Chicago will go into operation in 1928. This is the largest plant of its kind in the world and is built to treat 175 millon gallons per day. New York is contemplating the construction of a plant of equal size on Ward's Island.

Sludge Digestion. Digestion of settled sludge can be accomplished either in Imhoff tanks, in which the sludge compartment is below the settling compartment, or in separate digestion tanks. The latter are now being built in increasing numbers mainly be-

[67] Kadish, *Ind. Eng. Chem.*, **20**: 9 (1928).
[68] Wilson and Cramer, *Ind. Eng. Chem.*, **20**: 4 (1928).
[69] Mohlman and Palmer, *Eng. News-Record*, **100**: 147 (1928).
[70] Calvert, *Eng. News-Record*, **100**: 230 (1928).

cause of the possibility of heating the sludge by means of the gas produced by biological decomposition of the organic matter. Fischer and Quimby [71] have reported tests on the operation of such a plant at Antigo, Wisconsin. The digestor has a capacity of 34,000 cu. ft. for 5,600 connected population. An average of 0.64 cu. ft. of gas has been recovered per capita per day, all of which has been used to heat the sludge to an average temperature between 65° and 83° F. The organic solids were reduced to 25% of the initial weight by digestion.

Blew [72] gives operating results for the digestion tanks at Merchantville, New Jersey.

Gas is collected from the new Imhoff tanks at Newcastle, Pa., described by Donaldson. [73] Initial difficulties on account of acid sludge have now been overcome.

Industrial Wastes. Iron pickling wastes have been very detrimental to the operation of the new Imhoff tanks at Worcester, Mass., as reported by Lanphear. [74] The sludge production is excessive on account of the voluminous precipitate of ferrous and ferric hydroxides. The pH of the sewage averages 6.3, with a half-hourly fluctuation from 3.4 to 9.1. Rates of application to trickling filters are quite low because of the acidity and iron content of the settled sewage.

Similar difficulties in sewage treatment because of industrial wastes are reported by Mohlman. [75] Acid wastes from a paint factory containing copper, aniline dyes, sodium sulfate and lead were quite detrimental to the operation of an activated sludge plant even though diluted 50 or 100 times by a large volume of sewage. The presence of the wastes required doubled tank capacity and tripled air supply. Plans for elimination of wastes are described.

Coburn [76] reports that lime treatment of iron-pickling liquors is too costly and recommends addition of scrap iron to neutralize acidity, with recovery of ferrous sulfate.

Lime treatment of wastes containing acetic and sulfuric acids, calcium sulfate and tarry discharges from ethyl acetate stills is recommended by Snell and Snell. [77] Filtration of the lime sludge on an Oliver filter was successful, but the final effluent still had 6,000 p.p.m. oxygen consumed.

[71] Fischer and Quimby, *Public Works,* **59**: 97, 134 (1928).
[72] Blew, *Public Works,* **58**: 409, 468 (1927).
[73] Donaldson, *Public Works,* **59**: 164 (1928).
[74] Lanphear, *J. Boston Soc. Civil Eng.,* **14**: 450 (1927).
[75] Mohlman, *Water Works,* **67**: 163 (1928).
[76] Coburn, *Ind. Eng. Chem.,* **20**: 248 (1928).
[77] Snell and Snell, *Ind. Eng. Chem.,* **20**: 240 (1928).

Nelson[78] reports that treatment of packinghouse waste at Mason City, Iowa, by activated sludge has been somewhat unsuccessful on account of overload, very concentrated wastes and poor operation. Jenks and Levine[79] have reported experiments on the treatment of this waste by repeated circulations of waste and activated sludge in shallow streams over riffled surfaces, their so-called "stream-flow process."

Stream Pollution. An exhaustive report on a study of the pollution and natural purification of the Illinois River was issued during the past year by Hoskins, Ruchhoft and Williams[80] of the U. S. Public Health Service. This report included hydrometric studies and chemical and bacteriological analyses of samples collected daily from Lockport to the mouth of the river, a distance of 290 miles. The report is of general interest because it includes equations, based on the analytical results, which express the laws of self-purification of polluted waters and the death-rates of bacteria as affected by dilution, temperature and time.

Another interesting report, issued in 1927 by Crohurst and Veldee[81] of the U. S. Public Health Service, deals with the results of an investigation of the pollution of Lake Michigan off South Chicago and the Calumet District in Indiana. The work covered investigations of the discharge of sewage and industrial wastes into Lake Michigan and the resulting pollution as measured by analyses of 5,232 samples collected at 72 sampling stations over a period of 10 months. Only at a distance of from 5 to 8 miles offshore was water found which had a $B. coli$ index of less than 2 per 100 cc. Variable currents of polluted water could be traced for 15 or 20 miles, driven by winds to the water intakes of Chicago. The course of this distribution is shown by contours of bacterial counts. Sources of pollution were found to be mainly tributary to the Indiana Harbor Ship Canal and directly to the lake at Whiting and Hammond. Sewage treatment and disposal of wastes was strongly recommended.

[78] Nelson, *Can. Eng.*, **53**: 627 (1927).
[79] Jenks and Levine *Eng. News-Record*, **100**: 808 (1928).
[80] Hoskins, Ruchhoft and Williams, U.S. Public Health Service, Bull. 171 (1927)
[81] Crohurst and Veldee, U.S. Public Health Service Bull. 170 (1927).

Chapter XXIX.

Soils and Fertilizers.

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Upon the invitation of the United States government, 30 foreign nations sent delegates to the First International Congress of Soil Science which was held in Washington June 13 to June 22, 1927. During the sessions of the Congress, there was presented before the Commission for the study of soil chemistry a total of 55 papers of which 28 were from American workers. Of the papers involving chemical problems read before the other Commissions, approximately half were from American experiment stations and laboratories. The above statement will serve to indicate the relative output from the laboratories in this country in which chemistry and chemical methods are being applied to soil problems.

The extreme complexity of the soil offers a broad and at the same time a very difficult field for the application of chemical methods and technique. Many of the problems with which the soil investigator is concerned involve not only organic and inorganic chemical reactions but also the biological processes which are continuously in operation as the result of the activities of the microörganisms of the soil, such as bacteria, molds and fungi.

During recent years much of the chemical soil research has been concerned with soil colloids, base exchange and soil reaction. Of the soil materials, the colloidal fraction has received major attention because of the fact that the colloids are recognized as being much more active than the coarser fractions.

During the past year much attention has been directed to the application of electrodialysis to the study of base exchange phenomena. In the past the principle of electrodialysis has been applied to the study of blood serums, the separation of hexone

bases from proteins, the ultrafiltration of insulin solutions and the removal of electrolytes from colloidal solutions. Recently Mattson [1] applied electrodialysis to the determination of the replaceable bases in colloids obtained from soils and found a close agreement between his results and those obtained by the use of normal ammonium chloride, and that the quantity removable by electrodialysis was fairly definite.

Clark, Humfeld, and Alben [2] have suggested certain changes in the electrodes used by Mattson and have introduced a cooling system into the cell. In applying this method to different soils, these workers found that the time necessary for complete extraction varied with the soil type but that, as a rule, very little base or acid was removed after the first 24-hour period.

In his most recent work, Mattson [3] has studied the behavior of alumino-silicate mixtures and has investigated the conditions governing the formation of the different soil gels. He concludes that the adsorption of base by the natural gel embraces the adsorption of both ions, the OH as well as the cation, thus indicating true adsorption instead of the neutralization of an acid.

Bradfield [4] has employed a continuous flow through the anode chamber of a two-chamber type of cell, by means of which he has been able to extract the electrodialyzable bases from a 10 gm. sample of soil within four to eight hours. He points out the fact that practically all of the physico-chemical work on soils has been complicated by uncontrolled exchange reactions and that electrodialysis affords a convenient method for preparing "pure" sols upon which to work.

Rost [5] has made a study of the amounts of lime and of phosphoric acid removed from soils by electrodialysis, with a view of determining by this means the probable deficiencies of these plantfood materials. For some soils the results were promising but for two peat soils practically no correlation was found between the amount of lime removed and the response of alfalfa and sweet clover to applications of lime.

Roszmann [6] reports that electrodialyzed clay in the presence of calcium and sodium absorbed a maximum of phosphorus at a pH

[1] Mattson, *J. Agr. Research*, **33**: 553 (1926).
[2] Clark, Humfeld and Alben, *Soil Science*, **24**: 291 (1927).
[3] Mattson, *Soil Science*, **25**: 289 (1928).
[4] Bradfield, Proceedings First International Congress of Soil Science, 1928: *J. Am. Soc. Agron.*, **19**: 115 (1927).
[5] Rost, Proceedings First International Congress of Soil Science, 1928.
[6] Roszmann, *Soil Science*, **24**: 465 (1927).

of 3 to 4 and that above pH 9 there was no appreciable absorption.

Several papers which have been published throw some additional light on the nature of soil acidity. Bradfield [7] has called attention to the nondiffusible character of soil acidity and has shown that acid colloidal clay prepared by electrodialysis will not pass through a collodion membrane in sufficient quantity to significantly alter the pH of neutral distilled water.

Kerr [8] showed that alumino-silicic acids have certain properties in common with other colloidal acids. Alumino-silicic acids and tungstic acid each exert an influence on the pH of water suspensions which value is essentially dependent on the mass of the solid in suspension.

Anderegg and Lutz [9] made titration studies with neutral salts and found that colloidal clay behaves as a monobasic acid and appears to have a molecular weight of about 3500.

Magistad [10] has studied the action of aluminum and ferric iron salts in base exchange. He found that these salts remove the exchangeable bases present in soils but do not themselves become exchangeable. In this way they serve to destroy the exchangeable base capacity.

In addition to the work being done to determine the quantity of colloidal material in soils, several workers in this field are directing attention to the desirability of studying the chemical compositions of the colloidal fractions. Early in 1927 McCool [11] published the results of chemical studies of soil colloids and Holmes [12] has recently made a study of the variations in the chemical constitution of the colloidal material extracted from samples of soil collected from typical areas of the same soil type. Colloids isolated from several random samples of Leonardtown silt loam were found by Holmes to be fairly definite as to absorptive capacity for water vapor, ammonia gas and barium and in those inorganic constituents that were present in appreciable quantities. The content of SiO_2, Al_2O_3, Fe_2O_3, TiO_2, K_2O, MgO and combined water was fairly constant, while the content of MnO, CaO, SO_3, P_2O_5 and organic matter was much more variable.

Much attention continues to be directed to studies of the effect of soil reaction on the growth of crop plants, the chemical com-

[7] Bradfield, Missouri Agr. Expt. Sta., Bull. **256**: 94 (1927).
[8] Kerr, *J. Am. Soc. Agron.*, **20**: 309 (1928).
[9] Anderegg and Lutz, *Soil Science*, **24**: 403 (1927).
[10] Magistad, Univ. Ariz. Agr. Expt. Sta., Tech. Bull. **18**: 445 (1928).
[11] McCool, *J. Am. Soc. Agron.*, **19**: 289 (1927).
[12] Holmes, *J. Agr. Research*, **36**: 459 (1928).

position of the soil solution and the microbiological population. Powers [13] has shown by solution studies that alfalfa, Hungarian vetch, alsike clover and mint grow best in a slightly acid medium.

In certain regions the aluminum content of the soil, as related to crop injury, has been given considerable attention. Blair and Prince [14] have shown that acids and acid-forming materials added to the soil increase the amount of active aluminum in the soil solution and suggest that certain fertilizer practices may be responsible for the toxic conditions existing in certain soils.

During the year considerable attention has been directed toward the conditions affecting the availability of the phosphorus of the soil and its absorption by plants.

At the Illinois Experiment Station, Heck and Whiting [15] had previously shown that the oat plant is able to assimilate phosphorus from phytin and that this form of phosphorus was more readily assimilated than that of certain inorganic phosphates. More recently these workers have extended their study to include the clover plant. As in the case of the oat plant they find that red clover is able to utilize the phosphorus supplied in the form of phytin and that the presence of lime brings about a reversion of the soluble organic phosphorus to a less available inorganic form.

In studies of the availability of the phosphorus in the displaced soil solution and in water extracts of the soil, other workers have arrived at somewhat different conclusions.

Parker and Fudge [16] have recently modified methods of Denigès [17] and of Fisk and Subbarow [18] and applied them to the determination of the relative quantities of organic and inorganic phosphorus in the displaced soil solution and in soil extracts.

These methods are both based on the fact that a suitable reducing agent, when added to an ammonium molybdate solution of a certain acidity, will produce a blue color if the solution contains inorganic phosphate. The blue color is the result of the partial reduction of some of the molybdenum in the phosphomolybdate and, within certain limits, the intensity of the color is proportionate to the phosphate concentration.

Pierre and Parker [19] employed the modified method to study the availability of organic phosphorus to crop plants in work

[13] Powers, *Soil Science*, 24: 1 (1927).
[14] Blair and Prince, *Soil Science*, 24: 205 (1927).
[15] Whiting and Heck, *Soil Science*, 22: 477 (1926); 24: 17 (1927).
[16] Parker and Fudge, *Soil Science*, 24: 109 (1927).
[17] Denigès, *Compt. Rend. Acad. Sci.*, 171: 802 (1920).
[18] Fiske and Subbarow, *J. Biol. Chem.*, 66: 375 (1925).
[19] Pierre and Parker, *Soil Science*, 24: 119 (1927).

conducted at the Alabama Experiment Station. These workers determined the organic and inorganic phosphate in the displaced solution and in 1 : 5 water extracts of 21 soils from 9 States. Absorption and growth rate studies were then made to determine the availability to plants of the water-soluble organic phosphate. In the absorption experiments the plants absorbed all of the in-organic phosphorus from the solutions and soil extracts but none of the organic phosphate. Corn made no growth when organic phosphate in soil extracts was the only source of phosphorus but made good growth in other soil extracts containing inorganic phosphate.

These apparently discordant results raise an important question relative to phosphorus assimilation and serve to emphasize the importance and the desirability of devoting more time to fundamental studies of the soil solution and its relation to plant nutrition.

Teakle [20] has made an intensive study of the phosphate of the displaced soil solution in an attempt to show the effect of the various cations at different reactions, on the phosphate concentration of solutions. He concludes that the adsorption of phosphate is of minor importance and argues that the chemical properties of the compounds present were sufficient to account for the behavior of phosphates in the soil.

The use of sulfur as a soil amendment has been the object of study by several soil investigators, particularly in the Pacific Coast region. In his study of the effect of sulfur on the soils of California and Oregon, Powers [21] has found that heavy applications of sulfur result in increasing the soil acidity, which in turn causes an increase in the phosphate and iron content of the soil solution up to a certain point, after which the dissolved or replaced bases tend to precipitate these two ions from the soil solution. He concludes that sulfur in moderate amounts improves the reaction of arid soils for alfalfa nutrition. He finds that the addition of sulfur not only improves the reaction but also the structure of certain alkali soils by bringing about increased permeability.

McKibbin [22] has shown that soils low in total sulfur readily oxidize elemental sulfur to the sulfate form.

[20] Teakle, *Soil Science*, **25**: 143 (1928).
[21] Powers, Univ. of Calif., *Pub. in Agric. Sci.*, **5**: 119 (1927).
[22] McKibbin, Md. Agric. Expt. Sta., Bull. 296 (1928).

Chapter XXX.

Insecticides.

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The use of chemical compounds and mixtures for the control of insects continues to increase with the growth and extension of agriculture. There is now hardly a crop subject to the attack of insects which is not treated with chemicals to kill or repel them or restrict their destruction. In view of the large number of species involved, their different habits and the varied crops upon which they feed, insecticidal control measures are extremely diverse and new situations constantly demand new or modified procedure.

The present report covers the literature of insecticides issued during the past year (June 15, 1927, to June 15, 1928).

Arsenicals. Walker and Mills[86] and Walker[87] describe the preparation of a special Ca arsenate containing any desired proportion of As as As_2O_5 up to 57.6%, the theoretical ratio for $Ca_3(AsO_4)_2$. As_2O_3 is heated with precipitated chalk in the presence of excess air at 650° C. for 15 to 60 minutes. The process may be used to manufacture other arsenates from carbonates, and in some cases, from sulfates of the desired bases.

Van der Meulen and Van Leeuwen[82] have studied the action of excess $Ca(OH)_2$ on $PbHAsO_4$ in water. The result of long-continued action is the formation of Ca arsenate and a hydrate of PbO. In ordinary spraying practice, however, less than 1% of the $PbHAsO_4$ is decomposed. After all the lime has been carbonated by atmospheric CO_2, there is a material increase in quantity of soluble arsenic. Injury to peach foliage may be prevented by the addition of 3 lbs. slaked lime to 1.5 lbs. $PbHAsO_4$ in 50 gallons of water. Ginsburg[27] finds also that $CaCO_3$ reacts

directly with PbHAsO$_4$ in water to form soluble salts. Under the same conditions, sulfur had no appreciable action, but the addition of a commercial mixture of casein and lime resulted in the appearance of large quantities of soluble As$_2$O$_5$, which were apparently formed from the interaction of the CaCO$_3$ in the mixture with the PbHAsO$_4$. The addition of excess Ca(OH)$_2$ to water containing PbHAsO$_4$ retards but does not entirely prevent the formation of soluble As$_2$O$_5$, the minimum suppression being obtained with 6 to 8 lbs. Ca(OH)$_2$ in 50 gallons water containing 1.5 lbs. PbHAsO$_4$. Further studies have been undertaken by Ginsburg [25, 28] to find a substance which will prevent the formation of water-soluble arsenic in sprays containing PbHAsO$_4$, particularly those intended for use on tender foliage like that of the peach. ZnO was the most effective in this respect of the compounds used but serious plant injury due to the action of Zn attended its use. Fe$_2$O$_3$ prevented plant injury and also acted as an adhesive for the particles of PbHAsO$_4$, the latter property apparently being due to the electric charge on the Fe$_2$O$_3$ particles, which is opposite in sign from that on plant surfaces and to the absorptive properties for water, whereby the particles gain intimate contact with the water molecules of the leaf. Fe$_2$O$_3$ was also found to have value as an adhesive in a dust consisting of sulfur and PbHAsO$_4$. Greater adhesion of the dust particles to foliage was obtained when the Fe$_2$O$_3$ and lead arsenate were intimately ground together than when the Fe$_2$O$_3$ was mechanically mixed in the dust. Swingle [79] finds that dusts containing sulfur 80%, PbHAsO$_4$ 5% and Ca(OH)$_2$ 15% are chemically unstable and on long standing become dark in color, the result of the formation of PbS in the mixture. Varying quantities of Ca arsenate are formed depending upon the amount of the chemical change which has taken place. All the Ca(OH)$_2$ which does not react with sulfur is converted to CaCO$_3$ in 1 year or less. Although these chemical changes may not affect the insecticidal or fungicidal value of the dust in which PbS is formed, there is danger of plant injury from its use.

Beckwith and Driggers [4] have briefly described some of the factors which influence the use of PbHAsO$_4$ on cranberry bogs. The weak acids in bog water do not increase the solubility of this salt, but together with soluble iron compounds probably suppress its decomposition. Bog soils high in organic matter cause an appreciable formation of soluble As from PbHAsO$_4$, which is quickly removed from solution by the Fe compounds present.

Accumulative injury to plants was observed when $PbHAsO_4$ was used as a spray from year to year.

Yothers,[93] confirming previous work in South Africa and California, shows that $PbHAsO_4$, applied as a spray or dust to citrus trees, has a deleterious effect on the quality of the fruit, reducing the acidity and the soluble fruit solids.

The relation of arsenical spray residues on edible vegetable products to human health has long held the interest of public health officials, entomologists and manufacturers of insecticides and has had a directing influence upon insecticidal research. The question has lately been brought to a head by the ruling of the U. S. Food, Drug and Insecticide Administration that, beginning with the 1928 crop, arsenical residues shall not exceed the British tolerance of 0.01 grain As_2O_3 per pound of vegetable product (equivalent to 1.429 mg. As_2O_3 per kg.). Porter[65] has summarized the situation in so far as it affects the control of codling moth with arsenicals in the apple-growing sections of the United States. Many sections of the West and Northwest cannot with present methods and materials ($PbHAsO_4$) adequately control the codling moth without leaving arsenical residues which exceed the British tolerance. In the northeastern states control can be obtained without leaving excessive residues upon the fruit whereas in the Middle West, the situation is intermediate, the residues falling either above or below the tolerance. The various methods proposed to overcome this difficulty are discussed by Porter. They include removal of the residue, the use of shortened spray schedules, employment of dusts, contact sprays and other arsenicals and non-arsenicals which would be less objectionable from the health viewpoint than $PbHAsO_4$. Control by the use of bands, bait traps and codling moth parasites is also considered. A number of studies on the quantity of arsenical residue upon sprayed vegetable products have recently been published. Mac-Leod, Haley and Sudds[59] find that the quantity of residue on apples after 4 applications of $PbHAsO_4$ (3 lbs. in 100 gals. water) under Pennsylvania conditions always falls within the British tolerance. After the fruit has been handled preparatory to marketing only a trace of residue remains. Hartzell and Wilcoxon[36] report the following residues in mg. per kg. of fruit on apples which were given 5 applications of $PbHAsO_4$ (3.7 lbs. in 100 gals): As_2O_3, 0.042 to 0.193, av. 0.099; Pb, 0.155 to 1.80, av. 0.912. The ratio, Pb : As, found in these residues was considerably

higher than expected from the composition of the $PbHAsO_4$ used, probably due to the effects of atmospheric agencies whereby more As than Pb is dissolved and washed away by rains. Howard [47] finds that the arsenical residues on beans which have been treated with arsenicals at dosages recommended for the control of the Mexican bean beetle fall below the British tolerance after the beans have been prepared for the table.

Perhaps the most extensive series of experiments recently published on the relative effectiveness of arsenicals on insects is that by Walker and Mills [86] in which the cotton boll weevil (*Anthonomus grandis*) was the test insect. A number of metal arsenates, including Ba arsenate, Mg arsenate, Zn arsenate, $PbHAsO_4$ and Zn arsenite were equal to or of greater toxicity than commercial Ca arsenate and did not injure the cotton plant. A special Ca arsenate containing 24% As_2O_5 [87] was also equivalent in toxicity to ordinary Ca arsenate but at 10% As_2O_5 content the effectiveness of the preparation was reduced. A number of organic arsenic compounds, the methyl arsonates of Ba, Ca, Mg and Pb, Ca ethyl arsonate, and the phenyl arsonates of Ca, Mg and Pb, proved to be about equal in toxicity to the metal arsenates. The inorganic arsenic compounds, which were equal to Ca arsenate in their effects on the boll weevil but were definitely injurious to the cotton plant, include As_2O_3, As_2O_5, As_2S_5, Cu arsenite, Cu arsenate, Fe arsenite, Fe arsenate, Hg arsenite, Hg arsenate, Na_3AsO_3, Na_3AsO_4, Pb arsenite, Ca arsenite, Mg arsenate and Mg arsenite. The organic arsenic compounds included in this group were: Paris green, chlorovinyl arsenious oxide, methyl arsenious oxide, phenyl arsenious oxide, diphenyl arsenious sulfide, methyl arsenious sulfide, trimethylarsine sulfide and Na methyl arsonate. Organic arsenicals of very low solubility like diphenylamine chloroarsine, diphenylamine arsenious oxide and diphenyl arsenious oxide, were only slightly toxic. As_2O_3 adsorbed on coal dust was not an efficient substitute for Ca arsenate. Previous work with other insects was confirmed by showing that As_2O_3 is more toxic than As_2O_5 to the boll weevil. Although some of the organic arsenicals are equal in toxicity to Ca arsenate, it does not seem probable that they can compete in price with the metal arsenates. Porter [65] has tabulated some results on the comparative effectiveness of various non-lead arsenites and arsenates as stomach poisons for the codling moth. Placing $PbHAsO_4$ equal to 100%, the following order of toxicity is obtained: Ba arsenate $=$ $Ca_3(AsO_4)_2$, 100;

Zn arsenite = Ca arsenate, 75; Al arsenate = Zn arsenate = Mn arsenate, 67; Fe arsenate = Mg arsenate, 50. All except Fe arsenate caused more or less foliage injury. Fe arsenide, Ti arsenate, Cu arsenate and scorodite (native Fe arsenate) were practically worthless. Hough [46] compared the ability of codling moth larvæ from Grand Junction, Colorado, and Winchester, Virginia, to enter apples which have been sprayed with $PbHAsO_4$ (4 lbs. in 100 gallons water). In the former region a minimum of 7 or 8 sprays are recommended for control; in the latter region 3 and 4 sprays give excellent results. The Colorado larvæ showed a markedly superior ability over the Virginia larvæ to enter sprayed fruit. When the strains were crossed, the first generation larvæ of each cross were less resistant to $PbHAsO_4$ than the pure Colorado larvæ but more resistant than the Virginia larvæ. Snapp [74] gives the following order of effectiveness for a series of arsenicals used against the plum curculio: $PbHAsO_4 > Ba$ arsenate $> Ca_3(AsO_4)_2 > Zn$ arsenate $> Mg$ arsenate $> Mn$ arsenate $> Al$ arsenate. Scorodite was worthless. Flint and Frankenfeld [22] found Na_2AsO_3 nearly 100% effective in protecting seed wheat from insect attack.

Van Leeuwen [83] has studied the toxicity of $PbHAsO_4$ to the Japanese beetle. The area of leaf surface consumed decreased with increase of its As content; the average time from the ingestion of poisoned foliage to death varied from 68 to 88 hours and the average quantity of $PbHAsO_4$ eaten per beetle was 0.0035 to 0.015 mg. The results show that control of the Japanese beetle is obtained before the beetles have done any great injury to foliage with small doses of $PbHAsO_4$ applied as a spray. The cotton boll weevil, according to Grossman,[32] accumulates particles of Ca arsenate on the tip of the snout as it crawls about cotton plants which have been dusted with this compound. The poison is later ingested. In dusting, therefore, all plant surfaces should receive a coating of the arsenical. Walker and Mills [86] determined the arsenic (as As) in cotton boll weevils, which were poisoned with As_2O_3 absorbed on coal dust, as 0.00035 mg. per weevil whereas those poisoned with Ca arsenate contained 0.002 mg. As per weevil. The minimum lethal dose per weevil is given as 0.00013 mg. As, which is equivalent to 10 mg. As per kg. body weight and is believed to be somewhat too high. Fink [19] has studied the relation of arsenical poisoning in insects to the glutathione content of the tissues. Glutathione, a dipeptide of glutamic acid and cystein,

was present in the normal insects examined in amounts ranging from 0.18 mg. to 1.59 mg. After injection with H_3AsO_4, the average reduction in glutathione content of the tissues was 41% and 32% respectively. Although there is little doubt that arsenic has a specific affinity for the — SH group of reduced glutathione, it is admitted that other cell constituents may be involved in the action of arsenic upon insect tissue.

Hough [44] emphasizes the necessity of spraying both upper and lower leaf surfaces in the control of codling moth with $PbHAsO_4$, and in another publication [45] gives a detailed description of the arrangement of spray nozzles, types of spray outfits, capacity of pumps in volume per minute, length of hose, pressure and number of gallons of spray per tree necessary to do effective work. Sullivan [78] discusses the comparative effectiveness of $PbHAsO_4$ applied as a spray and a dust for the codling moth on apple trees. The cost of material favors the sprays whereas labor costs favor the dusts. Dusts are believed to be valuable as supplements for sprays in codling moth control. Porter [65] believes, however, that dusts are generally inadequate to control serious infestations of codling moth. Wakeland [85] recommends Ca arsenate applied as a dust or $PbHAsO_4$ applied as a spray for control of the snowy tree cricket on prune trees. Reeves [67] finds spraying with Ca arsenate the most effective control for the alfalfa weevil; dusting up to the present time has not given uniform results. Shotwell and Cowan [71] obtained favorable control of the Mormon cricket and the lesser migratory grasshopper with Na_3AsO_3 applied either as a spray or a dust. Clayton [10] reports favorable suppression of bacterial wilt and mosaic disease of cucurbits through control of the striped cucumber beetle with sprays containing $PbHAsO_4$ and Bordeaux mixture or dusts containing $PbHAsO_4$ and lime and Ca arsenate and gypsum. Longley [54] finds that arsenical sprays do not give efficient control of the apple tree leaf roller in Idaho, but that $PbHAsO_4$ and Paris green are more effective poisons for this insect than basic Pb arsenate or Ca arsenate.

Hamilton [33] has studied the adherence of $PbHAsO_4$ deposited on trees in the course of field spraying in relation to twig and leaf growth. The quantity of $PbHAsO_4$ per unit of leaf area decreased as the spraying season advanced in spite of successive spray applications until the growth of twigs and leaves slowed up when the arsenical residue rose abruptly. More $PbHAsO_4$ was deposited on the lower than upon the upper parts of the trees.

Fish oil according to Dozier [16] greatly increases the adhesion of particles in sprays containing $PbHAsO_4$, Bordeaux mixture and lime sulfur used to control codling moth and grape berry moth.

The use of arsenicals in insect baits is reported in a number of papers. Morgan and Chamberlin [60] find $PbHAsO_4$ and corn meal superior to Ca arsenate or Paris green in the same bait for the tobacco budworm, the last two compounds being injurious to tobacco foliage. Downes [15] uses arsenates of Ca and Mg, mixed with evaporated apple waste, as a bait for the strawberry rootworm. Todd [81] reports that a grasshopper bait consisting of As_2O_3 mixed with ground orange pulp may be preserved in cans and under these conditions will retain its effectiveness for long periods.

Leach [51] reports continued success with $PbHAsO_4$ mixed with the top soil as a preventive of damage to lawns and golf greens by larvæ of the Japanese beetle.

Fluosilicates. The fluosilicates are comparatively recent additions to the growing number of compounds which have found a use in the control of insects. Walker and Mills [86] and Walker [88] have prepared a special Na_2SiF_6 containing 80% of this compound and 20% SiO_2, which equals Ca arsenate in toxicity to the cotton boll weevil. It is obtainable commercially as a by-product of the manufacture of acid phosphate. In order to increase the adherence of this Na_2SiF_6 preparation to plant surfaces, the writers suggest the addition of a small quantity of starch, glue or casein. Fleming [20] has studied the physical properties and chemical reactions of 9 metal fluosilicates with reference to their use as insecticides. He finds that they are crystalline compounds more soluble in water than $PbHAsO_4$. The solubilities of the series, in parts per 1000 parts water were: $PbHAsO_4$ 0.16, $BaSiF_6$ 0.34, K_2SiF_6 0.94, $CdSiF_6$ 2.00, $CaSiF_6$ 3.11, Na_2SiF_6 7.14, $CuSiF_6$ 23.20, $SrSiF_6$ 32.00, $Al_2(SiF_6)_3$ 40.00, $ZnSiF_6$ 50.00. The fluosilicate particles do not settle readily on plant foliage and are easily removed by rains. They react with Bordeaux mixture, lime-sulfur solution and soap solutions and therefore are not adaptable for use in combined sprays. Marcovitch [57] recommends a neutral carrier such as flour, talc, sulfur and infusorial earth instead of hydrated lime for sodium fluosilicate dusts. In the presence of moisture, $Ca(OH)_2$ reacts with Na_2SiF_6 to form the soluble $CaSiF_6$, which may cause foliage injury.

The toxicity of fluosilicates to insects has recently been the subject of a number of publications. Walker and Mills [86] place

Na_2SiF_6, K_2SiF_6 and $BaSiF_6$ equal to Ca arsenate in toxicity to the cotton boll weevil and state that they produce little or no injury to the cotton plant. Fleming [20] finds that Na_2SiF_6, K_2SiF_6 and $BaSiF_6$ have the same order of toxicity as $PbHAsO_4$ for the Japanese beetle, whereas the fluosilicates of Sr, Zn and Ca are only moderately toxic and the fluosilicates of Cd, Al, and Cu are not efficient poisons for this insect. The first three compounds used by Fleming injured slightly the foliage of apple, peach and bean; the remaining 6 compounds were very injurious to these plants. When $BaSiF_6$ particles are coated with Pb oleate, the mixture is more toxic to the Japanese beetle than $PbHAsO_4$, is less injurious to foliage than the untreated compound and has excellent adhesive properties. Porter [65] states that $BaSiF_6$ equaled $PbHAsO_4$ in toxicity to the codling moth larvæ in laboratory experiments and that Na_2SiF_6 was nearly as good. In field experiments, the fluosilicates of Ba, Ca and Na gave comparatively poor results due to their inferior adhesive properties. $BaSiF_6$ is apparently not injurious to apple foliage at the concentrations used. Marcovitch [56, 58] has studied the toxicity of Na_2SiF_6 in water to mosquito larvæ (*Culex quinquefasciatus*), grasshoppers (*Melanoplus femur-rubrum*), and cutworms (*Feltia ducens*), to which it is more toxic than any of the arsenicals employed (Na_3AsO_3, Na_3AsO_4, Paris green, $PbHAsO_4$, Ca arsenate). For some other invertebrates (*Parameciam caudatum*, *Euglena* sp. and *Lumbricus terrestris*) it was more toxic than Na_3AsO_3. According-ing to Snapp,[74] Na_2SiF_6 is more toxic to the plum curculio than $PbHAsO_4$ and 7 other metal arsenates tested, but was very in-jurious to peach foliage and fruit. The addition of lime to a spray containing Na_2SiF_6 greatly decreased the toxicity. Flint and Frankenfeld [22] found $CaSiF_6$ and Na_2SiF_6 effective in preventing insect damage to seed wheat but the toxicity of these compounds to higher animals would greatly restrict their use in practice. Ingram [49] finds that Na_2SiF_6, applied as a dust, kills the striped blister beetle on soy beans whereas arsenicals repel the beetles without killing them. Hinds and Spencer [41] have investigated the possibility of controlling the sugar cane borer in sugar cane and corn by means of Na_2SiF_6 applied by airplanes and hand guns. At least 50% of the borers can be killed by this compound, whereas $PbHAsO_4$ and Ca arsenate are ineffective. The addition of 10% $Ca(OH)_2$ to the fluosilicate reduces foliage injury. Lyle [55] in-vestigated the relative effectiveness of Na_2SiF_6 and Paris green

in wheat bran as a bait for cutworms, the former always being
less toxic. Na_2SiF_6 generally gave better results than Ca and Mg
arsenates in a bait mixture containing evaporated apple waste for
the control of the strawberry rootworm, according to Downes.[15]

In view of the wide experimental use of the fluosilicates as
insecticides, interest has been aroused with respect to the possible
poisonous effects of residues of these compounds on fruits, vege-
tables and forage crops. Walker and Mills [86] have published some
values for lethal doses for rabbits and dogs. The ratio of lethal
doses for Ca arsenate and Na_2SiF_6 is $1:2.5$ for rabbits and $1:4$
for dogs. Marcovitch [56] determined the minimum lethal dose of
Na_2SiF_6 and K_3AsO_3 to rabbits by mouth as 120 mg. and 14 mg.
per kg. respectively. The estimated toxic dose for man is for
Na_2SiF_6 7.2 and for K_3AsO_3 0.84 g. In a later paper [58] the toxicity
to animals other than insects is discussed at some length. Morris [61]
fed an 800 pound horse 3 g. Na_2SiF_6 for three consecutive days
without ill effects to the horse, and determined the minimum lethal
dose of Na_2SiF_6 and Ca arsenate for the guinea pig as 0.05 g. and
about 0.017 g. respectively. He concludes that there is little danger
to livestock from forage crops dusted with Na_2SiF_6 if feeding is
permitted after rains have occurred.

Fluorides. Walker and Mills [86] found that BaF_2, PbF_2 and
cryolite ($AlF_3,3 NaF$) were equal to Ca arsenate in toxicity to
the cotton boll weevil and caused slight or no injury to cotton
plants. NaF, SrF_2 and CuF_2 were also highly toxic but produced
definite plant injury. In laboratory tests with codling moth larvæ,
Porter [65] noted that cryolite was highly toxic but that BaF_2, SrF_2,
MgF_2 and Al_2F_6 were of much lower toxicity. Marcovitch [56]
showed that NaF was less toxic to the mosquito, *Culex quinque-
fasciatus*, than either Na_2SiF_6, Na_3AsO_3 or Na_3AsO_4. He found
the relative effectiveness of several fluorides, arsenicals and
Na_2SiF_6 to this insect to be as follows: Na_2SiF_6 > PbF_2 > Paris
green > BaF_2 > CuF_2 > Ca arsenate > SrF_2 > CaF_2. To several
other invertebrates (*Paramecium caudatum*, *Euglena* sp. and
Lumbricus terrestris), NaF was more toxic than Na_3AsO_3 but
less toxic than Na_2SiF_6. Fulton and Brunson [24] used cryolite and
lime (1 to 2) with fair success as a dust to control the strawberry
leaf-roller. In a single test with a bait consisting of NaF and
evaporated apple waste, Downes [15] found NaF equal to Na_2SiF_6
and several arsenates in the control of the strawberry rootworm.

Wilson [90] gives results from the use of NaF in baits for grass-hoppers and the European earwig.

The toxicity of the fluorides to higher animals has been considered by Walker and Mills,[86] who show that the ratio of lethal doses of Ca arsenate and BaF_2 is $1:4$ for rabbits and $1:14$ for dogs, and by Marcovitch,[56] who determined the minimum lethal dose for rabbits to be 0.5 g. per kg. from which the toxic dose for man is estimated as 30 g.

Other Fluorine Compounds. Walker and Mills [86] appear to have been the first to test Na ferrofluoride and Ba fluochloride as insecticides. These compounds apparently have the same order of toxicity to the cotton boll weevil and the cotton plant as Ca arsenate.

Other Inorganic Chemicals and Mixtures. Flint and Frankenfeld [22] mixed seed wheat with various materials in an effort to prevent insect damage. $Ca(OH)_2$, gypsum, Cu carbonate, and Tennessee ball clay afforded considerable protection. Two other clays (Kentucky ball clay and bentonite) were less effective.

Dudley and Fluke [17] compared the efficiency of spraying and dusting with mixtures containing inorganic copper compounds for the control of the potato leafhopper. Bordeaux mixture was approximately equal in efficiency to dusts containing $CuSO_4$, $Ca(OH)_2$ and an inert filler. DeLong [14] obtained satisfactory control of the potato leafhopper on beans with Bordeaux mixture but the plants are subject to foliage injury, especially if $PbHAsO_4$ is added to the mixture. A dust containing $CuSO_4 . H_2O$ gave very promising results.

Newcomer and Yothers [63] found lime-sulfur solution of little value for the destruction of eggs of the European red mite and inferior to petroleum oil emulsions for those of the two-spotted mite. Sulfur applied as a summer spray or dust was unsatisfactory for the European red mite but controlled the two-spotted mite.

Bulger [6] has recently studied the possibilities of elemental sulfur as a soil insecticide. SO_2 and H_2S cannot be readily produced in soil in sufficient quantity to be effective against insects. The quantity of H_2SO_3 and H_2SO_4 necessary to kill ants (*Formica fusca subsericea*) in soil is greater than that readily obtained by the oxidation of sulfur in soil. Soil infesting insects (ants, white grubs, wireworms and cutworms) can withstand acidities as great as pH 2.8 which, if attained by the use of sulfur, would require more than 2000 lbs. per acre. Sulfur itself, applied to soil, is not

toxic to ants, grubs, root maggots or black peach aphis. It had no value as a carrier for nicotine sulfate or carbon disulfide.

In tests to evaluate a commercial preparation known as "fly salt," which contains free sulfur, NaCl, $CaCO_3$ and $Ca(OH)_2$ and which it is claimed will keep flies off cattle if taken internally, Aicher, Lush and Smith [1] found the preparation valueless. Various proprietary preparations have also been offered to rid poultry of external parasites (mites, ticks, insects) by administering them in the food or drinking water. The following compounds, known to be present in proprietary preparations offered for this purpose were tested by Parman, Abbott, Culver and Davidson: [64] $CaSO_3$, $CaSO_4$, CaS, CaS_2O_3, MgO, $MgSO_4$, Na_2SO_4, Na_2CO_3, KNO_3, Fe_2O_3, $Fe_2(SO_4)_3$, Fe_2SO_4, K_2TeO_3, K_2TeO_4, KI and S. They were all without effect upon the external parasites of poultry.

Compounds Containing CN. Woglum [91] discusses the re sults of an extensive series of experiments in the fumigation with HCN of citrus trees in Southern California for the control of black scale, red scale and other insects. In regions in which scale is particularly resistant to HCN, it is recommended that fumigation be followed by a petroleum oil spray. 28.4 g. of calcium cyanide (containing 30% HCN) were found to be equivalent in toxicity to 16 cc. of liquid HCN as a fumigant for these insects. Injury to citrus trees from HCN may vary widely from season to season. Quayle [66] also recommends HCN fumigation followed by an oil spray for resistant strains of red scale. Camp [7] describes methods, apparatus and some of the problems of research in HCN fumiga tion in Florida. Duration of exposure to the gas, temperature, pressure, atmospheric humidity, free moisture on plant surfaces and diffusion are factors of which, in so far as the effect on in sects and plants is concerned, little is known.

Brinley and Baker [5] have determined the toxicity of HCN to two species of aphids, one of thrips and two species of grain weevils. During the first 15 minutes of exposure, the lethal con centration of HCN is inversely related to the time but later it becomes independent of the time, the same concentration being required to kill in 1 hour as in 30 minutes. Susceptibility to this gas is directly related to the temperature and is more pronounced with short exposure periods. Humidity, however, has no effect on toxicity. The gas evolved from pure liquid HCN was more toxic to the insects than the gases resulting from the hydrolysis of Ca cyanide. The addition of small quantities of NH_3 and H_2S

to HCN lowers the toxicity of the mixture. When small quantities of methyl acetate are added to liquid HCN, the toxicity of the gas from the mixture is increased. It is believed that this result is due to the fact that the spiracles of the insect remain open under the influence of the gas mixture, whereas in pure HCN gas they are quickly closed and death comes more slowly.

Ca cyanide continues to be a useful insecticide dust. DeLong [14] obtained satisfactory control of the potato leafhopper and Little [53] killed 80% of squash bugs with applications of 42.5 g. Ca cyanide per hill of squash. Foliage was not injured except when the dust was applied to the leaves in large quantities.

Porter [65] states that Cu cyanide and Zn cyanide show considerable toxicity to codling moth larvæ and to apple foliage, and Walker and Mills [86] list Na cyanide, Ca cyanide and Hg cyanide as equal in toxicity to Ca arsenate for the cotton boll weevil but definitely injurious to the cotton plant.

In attempts to use NaCN in cane molasses as a poison bait for the adult onion root maggot, Baker and DeLong [3] observed that the bait was not poisonous. A chemical study lead them to believe that the NaCN reacts to form glucose cyanohydrin, which subsequently hydrolyzes to form NH_3 and $CH_2OH(CHOH)_5$ COOH.

Carbon Disulfide. Carbon disulfide emulsion has proved to be an effective insecticide under certain conditions for the larvæ of the Japanese beetle and some other insects. Some difficulties have been encountered in obtaining an emulsion that will remain homogenous over long periods and that can be poured and measured easily. Lipp [52] describes a preparation in which the emulsifier consists of a soap made of rosin, oleic acid and NaOH. More recently, Fleming [21] has proposed an improved formula for miscible CS_2. It is described as a mobile transparent liquid, sp. gr. 1.116, which will not form a heavy foam when shaken, which may be measured accurately, and which mixes with water in all proportions, forming a white emulsion. The formula is: CS_2 35 parts, alcoholic soap 65 parts, the soap being made from KOH, denatured alcohol, pale blown castor oil and water.

Herrick [40] obtained successful control of the centipede (*Scutigerella immaculata*) in greenhouses by means of miscible CS_2.

Weigel, Young and Swenson [89] describe an apparatus for the rapid volatilization of CS_2 for the treatment of bulbs infested with the bulb fly. The CS_2 is held in a copper pan which contains a

coiled copper tube through which water of the desired temperature is passed.

Strand [77] has compared the toxicity of CS_2 with CCl_4 and chloropicrin to the confused flour beetle (*Tribolium confusum*). Within the temperatures 10 to 35° C., chloropicrin (1 lb. per 1000 cu. ft. of space) is more toxic than 20 lbs. CCl_4 but less toxic than 15 lbs. of CS_2. A decrease in temperature lowers the toxicity of CCl_4 much more rapidly than that of CS_2 or chloropicrin. Plotting time to kill 100% of *Tribolium* against temperature, the result with these three compounds is not a straight line. The time increases at a greater rate toward the lower temperatures. Adsorption of the gases by the top layers of grain prevents rapid downward diffusion of the gases in bins, the amount adsorbed being greater the lower the temperature. Therefore temperature plays an important rôle aside from its relation to the toxicity of the fumigant or the activity of the insects.

Aliphatic Compounds as Fumigants. The demand for a fumigant to kill insects which attack seeds, cereals and other food products, fabrics, furs and similar materials has stimulated a search for chemicals which are effective, not dangerous to human beings, offer no fire hazard, are easy to use, do not affect the germination of seeds or milling quality of grains and are relatively low in cost. Cotton and Roark [11] found that a mixture of 3 parts ethylene dichloride and 1 part carbon tetrachloride meets these requirements for general fumigation in air-tight vaults. The dosage required is 6 lbs. of the mixture per 1000 cu. ft. of space at 29° C. and an exposure of 24 hours; at 18° C. 12 lbs. per 1000 cu. ft. are required to kill all the insects. Hoyt [48] recommends the use of this mixture at a dosage of 14 lbs. per 1000 cu. ft. of space for exposures of 24 hrs. at 29° C. Roark and Cotton [69] investigated the toxicity of 21 aliphatic chlorides as fumigants for insects which attack stored products. *tert.*-Butyl chloride was more toxic than the ethylene dichloride-carbon tetrachloride mixture but requires a greater dilution with carbon tetrachloride to render the mixture free from fire hazard and it also tends to break down and attack metals. Trichloroethylene is non-inflammable and fairly toxic to insects at temperatures above 26° C. None of the compounds tested seriously affected the germination of wheat at the concentrations employed. Vapors of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec.*-butyl, isobutyl, isoamyl and allyl formates were found by Cotton and Roark [12] to be toxic to rice weevils, clothes moths,

carpet beetles and furniture beetles. With the exception of the methyl and ethyl formates, these compounds can be rendered free from fire hazard by the addition of 60 to 75 volume % of carbon tetrachloride. They are not effective as fumigants below 24° C. They do not adversely influence the germination of wheat at concentrations which are toxic to insects. The effects on human food and upon metals have not been determined. Roark and Cotton[70] have also investigated the toxicity as fumigants for stored product insects of the lower alkyl esters of chloroformic (chlorocarbonic), chloro-, dichloro- and trichloroacetic, bromoacetic, α-bromo- and β-bromopropionic and β-chloropropionic acids. The methyl, isopropyl and ethyl chloroacetates appear most promising and are effective in commercial fumigation vaults at dosages of 1, 1.5 and 2 lbs. per 1000 cu. ft., respectively. The chloroacetic esters injure the germination of wheat and probably cannot be used in fumigating seed grain.

p-Dichlorobenzene. Snapp and Alden[75] recommend p-dichlorobenzene for the control of the peach borer in the southern peach belt. Trees 3 years old or younger may be injured by it, but it may be safely used on older trees. Similar recommendations are made by Thompson[80] for the control of western species of this insect which attack peach, plum, cherry and apricot. Siegler and Brown[73] dissolve p-dichlorobenzene in gasoline (28.4 g. in 50 cc.) and apply the liquid to the soil about the trunk of the tree. Advantages are claimed for this method over the use of the crystals. Fulinger[23] finds that p-dichlorobenzene is an excellent fumigant for centipedes in greenhouse soil, the crystals being placed just below the surface. In experiments with the cotton boll weevil, Walker and Mills[86] obtained a toxicity with p-dichlorobenzene equivalent to that of Ca arsenate but the compound was decidedly injurious to cotton plants. Hamilton[33] dissolved 1 lb. p-dichlorobenzene in 1 quart soluble pine-tar creosote and diluted the mixture with equal parts of water. When used as a spray, this mixture controlled all stages of the mottled poplar borer in willow without injury to the plant.

o-Dichlorobenzene. Snyder[76] has found o-dichlorobenzene effective in killing powder-post beetles in seasoned wood. Chandler[8] attempted to kill hibernating codling moth larvæ with an emulsion of o-dichlorobenzene without success.

Nicotine. Worthley[92] mixes basic compounds (Na_2CO_3, NaOH, K fish oil soap, Bordeaux mixture, lime-sulfur solution)

with sprays containing nicotine sulfate in order to release the nicotine, thereby increasing the toxicity of the solution to insects. The efficiency of lime-sulfur solution and of Bordeaux mixture for this purpose is increased by the addition of Na_2CO_3, but K fish oil soap was the most satisfactory of all the substances used. Woglum[91] recommends nicotine sulfate (1-1067) and a casein spreader as a spray for the citrus aphid. A nicotine-Ca(OH)$_2$ dust containing 2.5 to 3% nicotine is also used to control this insect. Headlee[38] finds that a mixture of petroleum oil emulsion and basic nicotine is highly toxic to apple aphids and the eggs of the European red mite. Childs[9] reduced thrips injury to apples with a spray mixture consisting of nicotine sulfate and petroleum oil emulsion. Hough[44] reports that nicotine sulfate is of little value as an ovicide for eggs of the red-banded leaf-roller. Porter,[65] in summarizing an extensive coöperative investigation of the codling moth, indicates that nicotine sulfate has produced variable results and that further work with this compound is advisable. DeLong[14] failed to control the potato leafhopper by spraying with nicotine and soap. Harman[34] finds a spray of nicotine sulfate and soap less effective than white oil emulsion for the peach cottony scale. Herbert[39] has compared the speed of spraying with nicotine sulfate and of dusting with nicotine dust. Spraying approaches dusting in time of operation at a lower cost for materials, which more than offsets the somewhat higher labor cost.

Walker and Mills[86] determined the effect of nicotine in the gaseous state on the cotton boll weevil. The weevils are killed in 30 minutes by a concentration of 5 mg. nicotine per liter; the toxic dose per weevil is estimated as 0.00075 mg. The order of relative toxicity of a number of gases for this insect is as follows: $H_2S >$ $HCN >$ nicotine $= AsH_3 > Cl_3CNO_2$.

Cinchona Alkaloids. Jackson and Wassell[50] have examined a large number of inorganic and organic compounds and mixtures of compounds in an effort to find a suitable material for moth-proofing fabrics and furs. Of those tested, the cinchona alkaloids and their derivatives proved to be remarkably effective. The fatty acid salts of the cinchona alkaloids are readily soluble in organic solvents like petroleum naphtha; other salts are water-soluble. They are inodorous, adhere to fabrics, can be put on evenly like a dyestuff, without harming the material and will not dust off. They are harmless to human beings. The quinidine salts appear to be the most economical of this group to use industrially. A process

in which these compounds have been employed has been in suc-
cessful commercial use for one year. The use of cinchona alkaloids
and their derivatives as insectifuges is patented. (U. S. 1,615,843,
Feb. 1, 1927.) Parman, Abbott, Culver and Davidson [64] were not
able to affect the abundance of external parasites on poultry by
daily internal administration of quinine sulfate to the hosts.

Pyrethrum. Van Leeuwen and Van der Meulen [84] show that
the addition of Na_2SiO_3 to a spray mixture containing the alco-
holic extract of pyrethrum flowers and Na oleate greatly increases
the toxicity of the preparation to the Japanese beetle. DeLong [14]
found that pyrethrum applied in a spray gave very satisfactory
results for the control of the potato leafhopper. Porter [65] reports
promising results with pyrethrum in laboratory and field tests
against the codling moth larva.

Derris. Porter [65] states that derris has given promising results
in field and laboratory experiments for the control of the codling
moth larva, and Daniel [13] found commercial derris extract (1 to
200) to be a successful control measure for the blackberry leaf-
miner, but it did not destroy the eggs of this insect. Hough [44] and
DeLong [14] found it ineffective against the eggs of the red-banded
leafroller and the adult of the potato leafhopper respectively.

Petroleum Oils. Considerable effort has recently been made
to extend the use of petroleum oils as insecticides, particularly to
insects which attack fruit trees. Green [31] has investigated the effect
of various fractions of lubricating oils, emulsified with potassium
fish oil soap and crude cresol, upon the San Jose scale and the
fruit tree leafroller. Although toxicity is exhibited by lubricating
oils having a wide distillation range, the fractions boiling within
the limits of 240 and 300° C. at 40 mm. pressure, show the
greatest lethal effect. Toxicity does not appear to be related to
viscosity and fractions from naphthene and paraffin base oils are
equally effective against these insects. Oils which have been
processed to remove the color completely are probably more effec-
tive than the unprocessed oils.

English [18] has recently made a study of the properties of petro-
leum oil emulsions which influence insecticidal efficiency. The
emulsifying agents used vary in wetting ability and therefore
cause variations in the effectiveness, especially with aphids.
Stability is an important factor in the efficiency of insecticide emul-
sions and is indicated to some extent by the size of the oil globules.
Stability is affected by the type of oil emulsified, the kind and

amount of the emulsifier and the quantity of water used in dilution. Increased effectiveness of an emulsion may or may not be associated with an increase in size of oil globules. Increased size of globules is the result of desirable qualities in an emulsion rather than the cause of insecticidal efficiency. The less stable an emulsion, the greater its effectiveness against scale insects. Because of its influence upon stability of the emulsion, a saturated oil may be more effective than an unsaturated oil. The quantity of oil adhering to an insect is dependent upon the wetting ability and the instability of the emulsion. Soaps and unsaturated oils tend to cause foliage injury.

Longley [54] finds that the eggs of the apple tree leafroller may be destroyed by a lubricating oil emulsified with calcium caseinate when applied during the dormant season. The specifications of the oil recommended are: Viscosity 90 to 250 secs. (Saybolt 100° F.), sp. gr. 0.87 to 0.93 at 20° C., volatility not over 2%. Injury to the tree may result from imperfect emulsification, improper dilution, or when the tree is weakened by excessive cold weather. Woglum [91] and Quayle [66] discuss the use of petroleum oil emulsion sprays supplemental to HCN fumigation for the control of citrus insects in certain regions of Southern California. The effects of various types of emulsions on insects and on citrus trees are described. Hough [44] reports poor results with lubricating oils for the destruction of eggs of the red-banded leafroller on apple. Newcomer and Yothers [63] were able to destroy red mites and their eggs on fruit trees in foliage with lubricating oil emulsion (0.5 to 0.67% oil) without injuring apple, pear, prune or cherry foliage. Peach foliage was invariably spotted by this treatment. Porter [65] in summarizing experiments with petroleum oil sprays for the control of codling moth larvæ on apple, states that they have given variable results and in some instances have injured fruit and foliage. Regan and Davenport,[68] however, cite experiments in which petroleum oils of a high degree of refinement and moderate or fairly high volatility have been successfully used with $PbHAsO_4$ to control the codling moth. The removal of spray residue is complicated by the use of this oil-arsenical mixture. Childs [9] finds petroleum oil emulsion ineffective against thrips on apple. Hartzell and Gambrell [35] recommended lubricating oils emulsified with Ca caseinate or with $CuSO_4$ and $Ca(OH)_2$ to control the pear psylla.

Highly refined, white petroleum oils are finding a special use as

sprays for trees in foliage due to their apparent less injurious effects on plant tissue than the unrefined oils. Harman [34] used a white oil emulsion (2% oil) in summer for the control of the peach cottony scale with good results. Severe injury to peach foliage occurred, however, when the oil emulsion was mixed with Bordeaux mixture or when the foliage retained sulfur residues. Mid-summer oil treatments are, in general, rcommended only in emergencies. Daniel [13] obtained promising results with white oil emulsions against the blackberry leaf-miner without damage to the foliage. Ginsburg [26] used white oil emulsions at oil concentrations as high as 0.75% on peach foliage with little or no injury, whereas the same concentration of ordinary lubricating oil caused from 10 to 40% of the leaves to drop. White oil emulsions containing 1 to 2% oil caused appreciable leaf drop; under the same conditions, ordinary lubricating oil removed 90% of the leaves and all the fruit. Ginsburg [29] later tested a number of petroleum, vegetable and animal oils on peach foliage; with the exception of a white medicinal petroleum oil and sperm oil all the oils produced injury at 2% oil concentration.

Siegler, Brown, Ackerman and Newcomer [72] have used a white oil emulsion on burlap bands to kill the entrapped codling moth larvæ.

Nelson [62] reports that when kerosene is applied to the body surface of insects, it penetrates the tracheæ to a greater distance than is generally supposed, the penetration probably being due to the surface tension of this liquid.

Interesting experiments on the use of fuel oil as a mosquito larvicide are reported by Ginsburg,[30] who observed that the addition of 1% cresol to the oil increases the spreading of the oil film on water and the toxicity of the mixture for the mosquito larvæ. Headlee and Miller [37] find that the oil film on polluted water may be broken by microörganisms which digest the hydrocarbons and by the evolution of H_2S produced by organisms in the water.

Other Organic Compounds and Mixtures. Walker and Mills [86] tested Ba salicylate, Mg salicylate, Ba benzoate, Ca benzoate, Pb tetraethyl, trichlorophenol, methylene blue and malachite green as stomach poisons for the cotton boll weevil. These compounds showed toxicity equal to or greater than Ca arsenate but caused definite plant injury.

Flint and Frankenfeld [22] find a mixture of crude creosote and $Ca(OH)_2$ very efficient in protecting seed wheat from insect

attack and safe to use as it is only slightly poisonous to most larger animals. Copper stearate also gave a large measure of protection. Several commercial organic mercury compounds, which have been used to control seed-borne fungi, have been found by Horsfall [43] to prevent damage to beans by bean weevils and to corn by the angoumois grain moth.

Siegler, Brown, Ackerman and Newcomer [72] and Alden and Yeomans [2] have obtained promising results with β-naphthol dissolved in lubricating oil as a treatment for cloth bands used to entrap and kill codling moth larvæ.

Headlee [38] destroyed 100% of eggs of the European red mite with a petroleum oil emulsion to which 0.5% crude cresol was added.

DeLong [14] found a cocoanut fatty acid emulsion unsatisfactory for the control of the potato leaf hopper on beans.

Hollister and Jacobs [42] attempted to control borers in trees by injecting into them nicotine sulfate, strychnine sulfate, aloes, aloin, thymol, acid fuchsin and As_2O_3. The results were negative.

Naphthalene, diethyl diselenide, antimony and potassium tartrate, potassium and sodium tartrate, capsicum, gentian, ginger, fenugreek, garlic, gum camphor, tobacco powder and nux vomica U.S.P. when taken internally, were entirely ineffective in ridding poultry of external parasites. [64]

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74. Snapp, *J. Econ. Entomol.,* **21**: 175 (1928).
75. Snapp and Alden, U.S. Dept. Agr., Tech. Bull. 58 (1928). 39 p.
76. Snyder, U.S. Dept. Agr., Bull. 1490 (1927). 46 p.
77. Strand. Minn. Agr. Expt. Sta., Tech. Bull. 49 (1927). 59 p.
78. Sullivan, *J. Econ. Entomol.,* **21**: 131 (1928).
79. Swingle, *J. Agr. Research,* **36**: 183 (1928).
80. Thompson, Ore. Bd. Hort. Bien. Rpt. 19: 125 (1927).
81. Todd, *J. Econ. Entomol.,* **20**: 844 (1927).
82. Van der Meulen and Van Leeuwen, *J. Agr. Research,* **35**: 313 (1927).
83. Van Leeuwen, *J. Agr. Research,* **34**: 1043 (1927).
84. Van Leeuwen and Van der Meulen, *J. Econ. Entomol.,* **20**: 603 (1927).
85. Wakeland, Idaho Agr. Expt. Sta., Bull. 155 (1927). 29 p.
86. Walker and Mills, *Ind. Eng. Chem.,* **19**: 703 (1927).
87. Walker, *J. Econ. Entomol.,* **21**: 165 (1928).
88. Walker, *J. Econ. Entomol.,* **21**: 156 (1928).
89. Weigel, Young and Swenson, U.S. Dept. Agr., Circ. 7 (1927). 8 p.
90. Wilson, Mo. Bull. Dept. Agr. Calif., **16**: 468 (1927).
91. Woglum, Calif. Fruit Growers Exchange. Bull. 4 (1927), 33 p.
92. Worthley, *J. Econ. Entomol.,* **20**: 615 (1927).
93. Yothers, *Citrus Ind.* (Fla.), **8**: 11 (1927).

Chapter XXXI.

Fermentation Industries.

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and

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The chief product of the fermentation industry, legal or other-wise, is ethyl alcohol. In keeping with the spirit of the day, alcohol manufacturers have consolidated. Four industrial alcohol com-panies merged to form The American Solvents and Chemical Corporation. Recently the formation of the American Commercial Alcohol Corporation brought together three producing companies.

The companies involved in these consolidations were single plant companies located in various cities. For these newly formed corporations, plants were selected with geographical locations favoring distribution of finished product. Further combinations bringing together other producing companies may be within the range of possibility.

By Act of Congress (March 3rd, 1927) the Bureau of Pro-hibition was created in the Treasury Department. This Bureau is charged with the administration of laws relating to the manufac-ture, sale and distribution of alcohol, thus relieving the Bureau of Internal Revenue of these duties. It is of particular interest to American chemistry that the first Commissioner of this Bureau, the Hon. J. M. Doran, is a chemist. It is encouraging to note that the Government is recognizing what chemists have long insisted upon, namely, that ethyl alcohol is an essential chemical com-modity and should be dealt with from that standpoint.

The fermentation industry, like every other industry, is a victim as well as a beneficiary of chemical progress. Fermentation lactic

acid has been an essential raw material in the manufacture of ethyl lactate. During the past year synthetic ethyl lactate has appeared on the market and threatens the fermentation product.

During the year, the commercial manufacture of synthetic methyl alcohol [1] from the gases generated in butyl alcohol fermentation was established. The collection and purification of fermentation carbon dioxide was extended to two alcohol plants during the year.

Research in the field of fermentation during the past year has been, in general, along lines previously well laid out. The investigations in European countries have dealt largely with the chemistry of the fermentation process including both the question of intermediate substances formed and the enzyme system involved in the changes. A large portion of the research has been of a purely scientific nature. In this country, work has had a closer relation to applications, either in the industries or in medicine.

Speakman [2] reports the results of experiments made with the object of adapting yeast to ferment galactose and finds that this is accomplished by so regulating the conditions that the yeast goes through a large number of reproductions in the presence of this sugar. The presence of glucose was found to stimulate the utilization of galactose. This work receives interesting corroboration from von Euler and Jansson,[3] who found that yeast did not acquire the property of fermenting galactose if just enough phenol was added to prevent growth nor when the growth was inhibited by high temperature. The authors were able to prove also that it is the enzyme complex and not the coenzyme that is modified in the process of adaptation.

Fulmer and Huesselmann [4] find that prolonged heating of certain culture media under pressure produces a yeast growth stimulant. Their experiments indicate that the stimulation is not due to a change in the pH of the solution but rather to the formation of some chemical substances which they think are allied to caramel.

An interesting study as to how fermentation proceeds in the presence of certain substances, with and without access of light, is reported by Macht.[5] Sodium benzoate added in a 1 : 1000 or 1 : 500 proportion caused only a very slight inhibition in the dark. In the light, however, this was increased 100 fold. Fluorescent

[1] Woodruff, *Ind. Eng. Chem.*, **19**: 1147 (1927).
[2] Speakman. *Can. Chem. Met.*, **10**: 229 (1927).
[3] von Euler and Jansson, *Z. physiol. Chem.*, 169: 226 (1927).
[4] Fulmer and Huesselmann, *Iowa State College J. Sci.*, **1**: 411 (1927).
[5] Macht, *Proc. Soc. Exptl. Biol. Med.*, **23**: 638, 639 (1926).

dyes were more actively inhibiting in the light than in the dark. It is worth while to note two other papers in which similar results are reported. Zeller [6] finds that X-rays stimulate the fermentation rate in small doses and have an inhibiting effect in larger doses. In the presence of certain substances, urea and ammonium tri-phosphate, for instance, the X-rays lose their effect. Warburg [7] shows a relation between the combination of CO with the respira-tory enzyme and light. He finds that short waves tend to break up the combination, and that long waves are without effect.

Abbott [8] reports that about one-half of the yeasts and yeast-like organisms tested by him were able to attack pentose when grown as pure cultures in a mineral nutrient solution in the presence of this sugar. In order for the yeast to act on the pentose, the acidity of the medium must be less than 5.0 pH. A similar relation be-tween fermentation of specific substances and the acidity is re-ported by Hägglund and Rosenqvist, [9] who find that pyruvic acid is not acted upon if the solution is even slightly alkaline. Hägglund and Ringbohm [10] also find yeast active toward certain substances only in definite pH ranges and state that the range varies with the substrate.

The vitamin content of yeast continues to make it a prominent material for dietary experiments. Vitamin B has now been shown to consist of two factors, one of which is more sensitive to de-struction by heat than the other. Sherman and Axtmayer [11] report on these substances, naming the antineuritic factor "F" and the thermostable factor "G." Autoclaved yeast is poor in "F," but rich in "G." Whole wheat is rich in "F" and poor in "G," while with milk the opposite is true. Chick and Roscoe [12] also report on the composite nature of the vitamin. A very interesting develop-ment in the vitamin field is reported by Knudson [13] and by Hess.[14] Yeast can be rendered strongly antirachitic by irradiation with cathode rays. The ergosterol from yeast when irradiated was found by Hess to be extremely active in preventing rickets. Cal-cification was brought about by as little as 0.002 mg. fed daily. Hess states this to be the smallest amount of any vitamin found

[6] Zeller, *Strahlentherapie*, **23**: 336 (1926).
[7] Warburg, *Biochem. Z.*, **177**: 471 (1926).
[8] Abbott, Missouri Agr. Expt. Sta., Bull. **85**: 29 (1926).
[9] Hägglund and Rosenqvist, *Biochem. Z.*, **180**: 61 (1927).
[10] Hägglund and Ringbohm, *Biochem. Z.*, **187**: 117 (1927).
[11] Sherman and Axtmayer, *J. Biol. Chem.*, **75**: 207 (1927).
[12] Chick and Roscoe, *Biochem. J.*, **21**: 698 (1927).
[13] Knudson, *Science*, **66**: 176 (1927).
[14] Hess, *J. Am. Med. Assoc.*, **89**: 337 (1927).

to exert a specific action. Petzold [15] states the therapeutically active factors in yeast to be as follows Vitamin B, phosphorus, lecithin, choline and an antidiabetic substance similar to insulin.

A food preparation made from yeast by growing the yeast in a malted flour, mixing with milk and then drying is covered by U. S. Patent 1,636,563.[16] This gives a yeasted malted milk. Another food preparation is described in U. S. Patent 1,603,472.[17] Yeast is mixed with a volatile antiseptic and autolyzed, the auto-lyzate is evaporated to a pastry consistency, the volatile antiseptic being driven off in this process, leaving an edible product.

Hixon and Balls [18] have been granted a patent on a method of activating yeast by treating it with non-toxic derivatives of fatty acids, such as sodium stearate, oleate, linoleate, laurate, palmitate or bromostearate. Very low concentrations are used—0.00000067 to 0.00004 mol of the substance employed per gram of yeast.

Two patents have been granted covering methods of making dry yeast. Hill and Givens [19] grow the yeast in a medium which consists of malted grains and nutrient salts. Before the medium is entirely exhausted, the growth is stopped by drying the entire mass. Balls [20] patents a method for drying yeast on cellulose from bran or rice polishings.

A patent on the preparation of cane molasses for yeast manu-facture was granted to Kusserow.[21] The process consists in grow-ing lactic organisms in the molasses, to which alkali has been added. The growth of these organisms is claimed to decompose colloids and form a precipitate, thus clarifying the molasses for subsequent use as a solution in which to propagate yeast. Balls [22] patents a method of growing press yeast in crude cane molasses. It is claimed that no treatment of the syrup is necessary. The process depends on the use of a special variety of yeast, *Saccharo-myces disjunctus*. This is a new yeast and Balls gives an identifi-cation method, using the agglutination technique employed in the identification of bacteria.

Morison and Reeser [23] contribute a paper to the technology of baking. Their work deals with the effects of impurities in

[15] Petzold, *Am. Med.*, **32**: 253 (1926).
[16] Hill and Givens, U.S.P. 1636563 (July 19, 1927).
[17] Kahn, U.S.P. 1603472 (Oct. 19, 1926).
[18] Hixon and Balls, U.S.P. 1651027 (Nov. 29, 1927).
[19] Hill and Givens, U.S.P. 1641676 (Sept. 6, 1927).
[20] Balls, U.S.P. 1643047 (Sept. 20 1927).
[21] Kusserow, U.S.P. 1642929 (Sept. 20, 1927).
[22] Balls, U.S.P. 1642192 (Sept. 13, 1927).
[23] Morison and Reeser, *Baking Technology*, **5**: 23 (1926).

the salt used in bread-making. They find that calcium and magnesium chlorides present as impurities in the sodium chloride decrease the fermentation period and increase the loaf volume. Paine, Birckner and Hamilton [24] continue work on the fermentation of fondant in chocolate coated creams with the consequent bursting of the candy. A method of preventing this by the addition of invertase to the fondant is described.

Ecker and Rimington [25] studied the toxic substances produced by the salmonella group of organisms and found that these substances could be precipitated by lead acetate. Tittsler and Lisse [26] studied the charge on bacteria and its relation to agglutinability and virulence. Winslow and Dollof [27] studied the action of certain cations on the growth of bacteria. It was found that a large number of cations (Na, K, Ca, Mg, Ba, Pb and Hg) stimulate in low concentrations and inhibit at higher concentrations. There is a large difference in the absolute magnitude of the effect, magnesium, for instance, being about 8 times as active as potassium or sodium. In some cases an additive effect was obtained from mixtures of salts where antagonism might have been expected. Attention is called to the fact that the hydrogen ion is enormously active as compared to the other positively charged ions. Several studies of the germicidal effect of NaOH have been made by Levine [28, 29] and co-workers. It was found that the action of the alkali was not related directly to the pH. The undissociated alkali was considered to have a direct antiseptic action. This was supported by the fact that, when other sodium salts were added to solutions of NaOH, the time necessary for the alkali to kill organisms was considerably decreased.

Pike and Smyth [30] were granted a patent on the production of butyl alcohol and acetone by the direct fermentation of a sterilized molasses mash containing no starchy material. The organism used is *Clostridium butyricum*. Marten, Sherrard, Peterson and Fred [31] describe a process for making lactic and acetic acids by the fermentation of waste liquors from wood. These liquors are first put through a fermentation for the production of alcohol; the slop from this process is used for the production of the organic

24 Paine, Birckner and Hamilton, *Ind. Eng. Chem.*, 19: 358 (1927).
25 Ecker and Rimington, *J. Hyg.*, 27: 44 (1927).
26 Tittsler and Lisse, *J. Bact.*, 15: 105 (1928).
27 Winslow and Dollof, *J. Bact.*, 15: 67 (1928).
28 Levine, Peterson and Buchanan, *Ind. Eng. Chem.*, 20: 63 (1928).
29 Levine, Buchanan and Toulouse, *Iowa State College J. Sci.*, 2: 19 (1927).
30 Pike and Smyth. U.S.P. 1655435 (Jan. 10, 1928).
31 Marten, Sherrard, Peterson and Fred, *Ind. Eng. Chem.*, 19: 1162 (1927).

acids. Matheson, Boyer and Warren [32] describe a method for the control of certain undesirable fermentations in Swiss cheese. Oxygen was used to check these fermentations, thus indicating them to be caused by anaërobic organisms.

Clarke [33] reports work on the official method of vinegar analysis. Collaborative work on this method indicated that the procedure for P_2O_5 and SO_3 needed revision, but good agreement between different analysts were obtained on non-volatile reducing substances. Stein [34] was granted a patent on an apparatus for determining alcohol. The apparatus is similar to an ebullioscope.

Rogers [35] catalogues the cultures in the American type culture collection. Bacteria, yeasts, molds, etc., are available for public distribution. The John McCormick Institute for Infectious Diseases supplies these cultures at $1.00 each.

The following books on fermentation have appeared in Great Britain and Europe. They are given here for the convenience of anyone interested in recent publications covering the subject of fermentation as a whole.

Handbuch der Gahrungsbakteriologie, Berlin, Paul Parey. 602 pp.

W. Henneberg. Handbuch der Gahrungsbakteriologie. 2nd Ed. Berlin, Paul Parey. 404 pp.

M. Shoen. Les problemes des fermentations (Les faits et les hypotheses). Paris, Masson et Cie. 199 pp.

Chimie analytique des industries des fermentations, Vol. 1, Gaud.

C. A. Mitchell. Vinegar. Its manufacture and examination, 2nd Ed. London, Chas. Griffin & Co., 211 pp.

[32] Matheson, Boyer and Warren, *J. Dairy Sci.,* **10**: 53 (1927).
[33] Clarke, *J. Assoc. Official Agr. Chem.,* **10**: 490 (1927).
[34] Stein, U.S.P. 1658950 (Feb. 14, 1928).
[35] Rogers, Catalogue printed by Waverly Press, Baltimore, Md., may be obtained from John McCormick Institute of Infectious Diseases, Univ. of Chicago, Chicago, Ill.

Chapter XXXII.

Survey of American Pharmaceutical Chemistry.

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Plants and Vegetable Drugs. Additional interest in the drug Ephedra has been shown. Black and Kelley [1] describe the isolation of pseudoephedrine from *Ephedra alata;* Feng and Read [2] discuss its assay, and Read and Liu [3] report an investigation of botanical sources of ephedrine and pseudoephedrine. Williams [4] describes a satisfactory method of assay.

Gordon [5] continues an investigation from the Wisconsin Phar-• maceutical Experiment Station on peppermint oil; and Mellanoff [6] describes in detail the properties and constituents of the oil from seeds of digitalis. He [7] also describes an extensive investigation on the properties, isolation and quantitative determination of digitonin.

Clark [8] continues investigations upon the constituents and extraction of *Ceanothus americanus.* Sievers [9] goes extensively into methods of extraction of volatile oils from plant materials and the production of these in the United States.

The results of a four year period of observation of a considerable number of fluid extracts and tinctures prepared and stored under different conditions in order to learn something about the causes of precipitation in such medicinal products is reported by Scoville [10] For the purpose of determining the best method of

[1] Black and Kelley, *Am. J. Pharm.,* **99**: 748 (1927).
[2] Feng and Read *J. Am. Pharm. Assoc.,* **16**: 1034 (1927).
[3] Read and Liu *J. Am. Pharm. Assoc.,* **17**: 339 (1928).
[4] Williams, *J. Am. Pharm. Assoc.,* **17**: 430 (1928).
[5] Gordon, *Am. J. Pharm.,* **99**: 524 (1927)
[6] Mellanoff, *Am. J. Pharm.,* **99**: 549 (1927).
[7] Mellanoff, *Am. J. Pharm.,* **99**: 390 (1927).
[8] Clark, *Am. J. Pharm.,* **100**: 240 (1928).
[9] U.S. Dept. Agr., Tech. Bull. No. 16 (1928). 35 p.
[10] Scoville, *J. Am. Pharm. Assoc.,* **16**: 1136 (1927).

standardization and stabilization of fluid extracts of nux vomica, gelsemium, and veratrum, Swanson and Hargreaves [11] have conducted an extensive investigation with particular reference to the effect of the pH value upon the stability of the active principles.

With a similar idea in mind, Krantz and Slama [12] have investigated the effects of pH concentration upon compound tincture of gentian.

Clark [13] records a study of the toxic substance of cotton-seed gossypol, and presents a method for preparation and purification, together with a determination of its molecular weight, and data upon various derivatives, also upon its physiologic effect.

Gland Products. The dialysis of pituitary extracts and the indications therefrom as to molecular weights of the pituitary active principles are treated by Kamm. [14]

The outstanding research reported during the past twelve months is that of Kamm, Aldrich, Grote, Rowe, and Bugbee [15] upon the separation and identification of two active principles from the posterior lobe of the pituitary gland. Their results quite conclusively prove the presence of two distinct active principles, the one known by the technical name of α-hypophamine and commercially as oxytocin, which presents the oxytocic effect of the posterior lobe with only a very slight amount of pressor activity, while the other, β-hypophamine, known also as vasopressin, presents the pressor activity with almost no trace of oxytocic effect. The diuretic and anti-diuretic action of the gland appears to be directly associated with the pressor substance.

Further investigations of anti-diabetic material from pancreas are reported and a patent has been taken out by Murlin [16] on a method for producing anti-diabetic substance in form to be given orally.

Analytical. The possible use of characteristic fluorescence of many different substances when exposed to ultraviolet light has previously been recommended, especially from some European sources, as an analytical procedure of probable usefulness. Wimmer and Goodman [17] report a series of experiments on the detection of impurities and evidence of adulteration in a wide

[11] Swanson and Hargreaves, *J. Am. Pharm. Assoc.*, **17**: 23 (1928).
[12] Krantz and Slama, *J. Am. Pharm. Assoc.*, **16**: 1156 (1927).
[13] Clark, *J. Biol. Chem.*, **75**: 725 (1927).
[14] Kamm, *Science*, **67**: 199 (1928).
[15] Kamm, Aldrich, Grote, Rowe and Bugbee, *J. Am. Chem. Soc.*, **50**: 573 (1928).
[16] Murlin, U.S.P. 1646553 (Oct. 25, 1927).
[17] Wimmer and Goodman, *Am. Perfumer*, **22**: 567 (1927).

variety of substances. The results so far are interesting but not such as to give this method of analysis an established form.

Emery,[18] from the Food, Drug and Insecticide Administration, discusses methods of assay for aspirin, cinchophen and caffein in admixture.

Von Oettingen, Sollmann and Schweid[19] discuss the physical and chemical properties of bismuth sodium citrate and bismuth sodium tartrate, with particular reference to the effect of pH value on the character of solutions.

Miscellaneous. The use of mucic in place of tartaric acid in granular effervescent salts, and other pharmaceuticals, has been studied by Blicke and Powers.[20]

A study of some length of the calcium salt of 5-iodoguaiacol and 5-iodoguaiacol carbonate is described by Greenbaum.[21]

Greenbaum[22] also presents a survey of various organic gold compounds intended for internal use, which includes an interesting bibliography.

A study of the effect of various compounds in preventing the development of rancidity in fats and oils, with particular reference to ointments, is presented by Husa and Husa.[23] Hydroquinol is the most effective of the substances tried for this purpose, while salicylic acid, acetylsalicylic acid, β-naphthol, liquefied phenol, dl-alanine, pyrogallic acid, and resorcinol are of no effect. The toxicity of an impurity which may be present in cinchophen which will yet pass in a satisfactory manner all the tests prescribed by the U. S. P., has been investigated at some length by Hatcher.[24] The substance is γ-anilino-γ-phenyl-n-butyric acid. It was found that this impurity is quite low in toxicity.

[18] Emery, *J. Am. Pharm. Assoc.* **17**: 18 (1928).
[19] von Oettingen, Sollmann and Schweid, *J. Am. Pharm. Assoc.*, **17**: 540 (1928).
[20] Blicke and Powers, *J. Am. Pharm. Assoc.*, **16**: 1146 (1927).
[21] Greenbaum, *Am. J. Pharm.*, **100**: 112 (1928).
[22] Greenbaum, *J. Am. Pharm. Assoc.*, **17**: 232 (1928).
[23] Husa and Husa, *J. Am. Pharm. Assoc.*, **17**: 243 (1928).
[24] Hatcher, *J. Am. Pharm. Assoc.*, **17**: 557 (1928).

Chapter XXXIII.

Structural Cements.*

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The literature covering the chemistry of hydraulic cements in America is exceptionally meager. This is due largely to the fact that cement is a raw material used by the engineer to produce another commodity—mortar or concrete—having certain definite physical properties. The cement is therefore evaluated practically entirely by physical properties and not by chemical properties. The raw materials, usually clay and limestone, used in making by far the most widely used of these cements, portland cement, contain many impurities. Hence the finished product is a hetero- geneous mixture of quite a number of chemical compounds. Furthermore, it is produced under conditions that to date have not received the needed attention of teachers or investigators. In none of our educational institutions is any particular emphasis given to the study of the fundamentals involved in the reactions of inorganic, non-metallic compounds at temperatures above 1200° C., or to the study of the reactions of the same kind of com- pounds with small quantities of water. As a consequence cement chemists have not been trained to be other than analysts to control the carrying out of a process intended to produce a commodity having certain physical properties. Until recently, furthermore, the industry has had its attention drawn so much to meeting in- creased demands for more output that it has not taken the time to devote much attention to fundamental research or to chemical control of production problems.

The Portland Cement Association, a trade association composed of manufacturers of portland cement in the United States, feel- ing the need of coördinated fundamental research as to what port-

land cement is, how conditions of manufacture affect its constitution, how changes in composition and constitution affect the physical qualities of the concrete made from the cement and what are the products of the reaction of cement with water, established a group of research associates at the Bureau of Standards to study these problems. This has been in effect since June, 1924. Since the previous volumes of the Annual Survey of American Chemistry have not contained a chapter devoted specifically to structural cements, limes and plasters, it would seem desirable to cite all of the publications of these research associates, although a number have appeared previous to the period covered by the present volume. These constitute practically all of the publications in the period in American literature, of American origin, dealing with the chemistry, pure and applied, of cements. By far the greater number of publications appearing in American literature covering these topics are of foreign origin.

Constitution of Portland Cement. The following papers covering studies on the constitution of portland cement have appeared from the Portland Cement Association Fellowship at the Bureau of Standards: "Studies on the system calcium oxide— ferric oxide—silica," [1] "Determination of uncombined lime in portland cement," [2] "Studies on the system lime—alumina—silica. The composition $8CaO + Al_2O_3 + 2SiO_2$," [3] "X-ray diffraction measurements on some of the pure compounds concerned in the study of portland cement," [4] "Further studies on portland cement compounds by the X-ray diffraction method," [5] "The combination of lime in portland cement compounds," [6] "Studies on the system calcium oxide—alumina—ferric oxide," [7] and "Equilibrium studies on alumina and ferric oxide and on combinations of these with magnesia and calcium oxide." [8]

In the first paper cited Hansen and Bogue [1] did not find any indications of the existence of any ternary compounds but noted the existence of a mono- and dicalcium ferrite. They also obtained further evidence of the existence of tricalcium silicate.

A series of studies of methods [2] for determining the lime remaining uncombined in compositions conforming to that of portland cement resulted in suggesting a method which consisted of treating the finely ground sample with a solution of glycerol in absolute alcohol, heating to boiling and titrating while hot with

[1] Hansen and Bogue, *J. Am. Chem. Soc.*, **48**: 1261 (1926).
[2] Lerch and Bogue, *Ind. Eng. Chem.*, **18**: 739 (1926).

an alcohol solution of ammonium acetate. Phenolphthalein is used as an indicator.

A great many German investigators believe that the alumina in portland cement is combined with the silica to form a ternary compound, $8CaO + Al_2O_3 + 2SiO_2$. A very thorough study of compositions in which such a compound might form was made in collaboration with Dyckerhoff,[3] who happened to be in this country, and who was one of the German investigators who be-lieved in the existence of this compound. The investigation showed that this compound did not exist and that the fiber-like crystals previously reported to be $8CaO + Al_2O_3 + 2SiO_2$ were in reality tricalcium silicate. This was confirmed not only by petrographic methods but also by X-ray diffraction patterns of this supposed compound. The X-ray patterns further showed that this supposed homogeneous compound was not homogeneous, containing other compounds than the tricalcium silicate.

In further X-ray study the constants of the compounds $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $Ca(OH)_2$, Al_2O_3, Fe_2O_3, CaO, $CaCO_3$, and SiO_2 have been determined and are reported by Harrington[4] in the fourth paper cited above. Studies were also made by Hansen[5] of the compounds $3CaO.SiO_2$, and gamma and beta $2CaO.SiO_2$.

Hansen and Bogue[6] have investigated particularly the replacement of lime by small amounts of soda or potash, the replacement of alumina by small amounts of ferric oxide and the replacement of lime by magnesia in two typical lime—alumina—silica compositions approaching those used in the making of portland cement. Their study was devoted to the relation between the amount of lime remaining uncombined in the presence of these additions, at various heating temperatures. It was found that the amount of lime that would remain free was very materially affected by the different substitutions. The authors attempt to explain why the various replacing oxides have different effects in this respect.

Hansen, Brownmiller and Bogue[7] confined their study of the system calcium oxide—alumina—ferric oxide to a portion of the system which might occur in portland cement mixtures. They found that a ternary compound of the composition $4CaO.Al_2O_3.Fe_2O_3$ was present in part of the system. Its melting point and

[3] Hansen, Dyckerhoff, Ashton and Bogue, *J. Phys. Chem.*, **31**: 607 (1927).
[4] Harrington, *Am. J. Sci.*, **13**: 467 (1927).
[5] Hansen, *J. Am. Ceram. Soc.*, **11**: 68 (1928).
[6] Hansen and Bogue, *Ind. Eng. Chem.*, **19**: 1260 (1927).
[7] Hansen, Brownmiller and Bogue, *J. Am. Chem. Soc.*, **50**: 396 (1928).

optical properties are given. $2CaO.Fe_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$ form a complete series of solid solutions. The melting relations and optical properties of these are also given. Both monocalcium aluminate and monocalcium ferrite form limited solid solutions with each other. It was also found that in this system $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ have higher indices of refraction than when they occur in a binary system.

Hansen and Brownmiller [8] have amplified their work by determining the planar spacings and relative intensities of the lines in the X-ray diffraction patterns of the oxides which they studied and of $MgO.Al_2O_3$ and $MgO.Fe_2O_3$. They also in this investigation studied the changes in the crystalline structure produced by the heating of alumina and ferric oxide from several sources. They found two new compounds, $4CaO.2MgO.Al_2O_3.Fe_2O_3$ and $2CaO.MgO.Fe_2O_3$. The melting points and optical properties of these are also presented. They also found that up to two per cent of alumina in $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ can be replaced by Fe_2O_3 and form homogeneous preparations. They found furthermore a very large series of solid solutions between a number of the compounds in this system.

Draffin,[9] making use of some data presented some time ago from the Bureau of Standards on the strength of the two silicates and one aluminate of lime present in portland cement, has calculated what should be the strength in tension of some portland cements according to their calculated constitution. He found the computed strength to be lower than the actual strength.

Bates [10] has presented data showing the strength at the end of ten years of concretes made from cements which had been manufactured so as to give magnesia contents from about 1% up to 25%. The results show that cements of good quality can be produced with care in manufacture containing as much as 6% magnesia. These would have lower strength than what is demanded of standard portland cement at the early ages, but would show good gain in strength with age. Ten year concrete made from cements containing as much as 14% magnesia showed no marked disintegration.

Hydration. Ashton and Wilson [11] have prepared crystals of $Ca(OH)_2$ and determined their optical and X-ray characteristics.

8 Hansen and Brownmiller, *Am. J. Sci.*, **15**: 225 (1928).
9 Draffin, *Proc. Am. Soc. Testing Materials*, **27**, pt. II: 313 (1927).
10 Bates, *Proc. Am. Soc. Testing Materials*, **27**, pt. II: 324 (1927).
11 Ashton and Wilson, *Am. J. Sci.*, **13**: 209 (1927).

These are valuable data to all studying the hydration of portland cement in view of the fact that this hydroxide is formed through the hydrolysis of the silicates present in portland cement. They found that (1) calcium hydroxide crystallizes in the hexagonal system usually as plates or short hexagonal prisms, with perfect cleavage parallel to the face (.0001); (2) the refractive indices are $\omega = 1.574 \pm 0.003$, $\varepsilon = 1.545 \pm 0.003$ for sodium light. Birefraction is 0.029. Specific gravity 2.230 ± 0.005. Interference figure is uniaxial negative. Lattice constants are $a_0 = 3.579$Å, $c_0 = 5.028$Å. The unit cell contains one molecule; and (3) the crystals are non-hydrated $Ca(OH)_2$, fairly stable in air, only slowly dissolved by water. When exposed to moist air or to water containing carbon dioxide they tarnish in a short time, becoming covered by a crust of carbonate.

Lerch and Bogue [12] found in the studies of the compounds $3CaO.SiO_2$, $\beta 2CaO.SiO_2$, $\gamma 2CaO.SiO_2$, $5CaO.3Al_2O_3$, $3CaO.Al_2O_3$ and $2CaO.Fe_2O_3$, that each of the aqueous solutions underwent hydrolysis, as indicated by the presence of hydroxyl ions. As measured by the pH of the resultant solutions the aluminates come to equilibrium more rapidly than the silicates and the ferrite. The OH ion concentration necessary to prevent hydrolysis is different for the several compounds, as follows:

	pH
$5CaO.2Al_2O_3$	11.7
$3CaO.Al_2O_3$	12.3
$2CaO.Fe_2O_3$	13.0
$3CaO.SiO_2$	
$\beta\ 2CaO.SiO_2$	13.7
$\gamma\ 2CaO.SiO_2$	

The pH of saturated $Ca(OH)_2$ at $30°$ C. is 12.4. Hence the aluminates do not hydrolyze in such solutions, the ferrite hydrolyzes slightly and the silicates hydrolyze to a greater extent. If the soluble products are intermittently removed, the silicates will hydrolyze eventually to hydrous silica, the aluminates to hydrous alumina and the ferrite to hydrous ferric oxide. In each case $Ca(OH)_2$ is the other product. If the soluble products are not removed, hydrolysis will proceed to the formation of $Ca(OH)_2$ and a less basic silicate, aluminate or ferrite. The composition of the end products in this case will be determined by the OH ion concentration and the amount of available water. In

[12] Lerch and Bogue, *J. Phys. Chem.*, 31: 1627 (1927).

the presence of a large amount of saturated lime water, the silicates seem to go largely to a composition which may be represented by $CaO.SiO_2.aq.$, and the aluminates to a composition $3CaO.Al_2O_3.aq.$

General. The coöperative research with the Portland Cement Association at the Bureau of Standards has led to preparing three papers of general interest. The first of these by Bogue [13] presents a digest of the literature on the constitution of portland cement clinker. The second paper by Bogue [14] presents a digest of reasons for the necessity of carrying on research on the fundamentals of portland cement and the value of such research to the engineer using cement. Brownmiller [15] shows how optically clear selenium may be prepared and describes its use in the determination of the indices of refraction of the high index components existing in portland cement.

Jakkula [16] presents some results which he obtained in determining the amount of heat evolved and the temperature reached during the setting of high alumina and portland cements. There is no connection between the data presented and the constitution of the cement in question. Levens [17] shows that the shrinkage of concrete is greatly increased when calcium chloride, to the extent of 1 to 6%, is added. This is apparent even when the optimum amount of chloride, 2 to 4% by weight of cement, is used. No data are given to show the character of the cements tested. Some experiments [18] carried on at the Bureau of Standards on the volume changes produced in 32 different portland cements showed that neat bars 1 by 1 by 6 inches in size showed expansions varying from 0.0 to 0.061% when subjected to the action of steam for 5 hours at the expiration of the first 24 hours of their life.

New Developments. New capital, with consequent new plants, is still being attracted to the industry notwithstanding that there is already an apparent over-development. These new plants or special features of these, which are found described in practically every issue of Rock Products [19] or the Cement Mill section of Concrete, [20] indicate trends in refinement of plant assembly and operation which in turn indicate a cheaper and a better

[13] Bogue, *Concrete,* 29, no. 1: 14 (1926) to 30, no. 2: 36 (1927).
[14] Bogue, *Proc. Am. Soc. Testing Materials,* 26 pt. II: 403 (1926).
[15] Brownmiller, *Am. Mineralogist,* 12: 43 (1927).
[16] Jakkula, *Eng. News-Record,* 99: 995 (1927).
[17] Levens, *Eng. News-Record,* 99: 912 (1927).
[18] *Rock Products,* 30, no. 25: 57 (1927).
[19] *Rock Products,* 542 S. Dearborn St., Chicago, Ill.
[20] *Concrete,* 139 N. Clark St., Chicago, Ill.

product. Closer study of the efficiency of plant equipment is indi-
cated in the new types and better construction of grinding equip-
ment and rotary kilns. It is of interest to note that one mill has
been put into operation and another is about completed in which
the greater part of the equipment, including the tube mills and
the rotary kilns, has been imported. The use of the wet process
still continues to gain favor as do methods for the recovery,
either through waste heat boilers or recuperators, of heat formerly
lost in kilns. However, it should be noted that several new mills
have found it more economical to buy power and operate largely
during off-peak-load periods with power produced by large power
corporations than to install waste heat recovery plants of their
own. The handling of the powdered raw material, coal and
finished cement in other than closed pump circuits is rapidly
disappearing.

Chapter XXXIV.

Lime and Gypsum.*

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A review of the 1927-28 literature relative to lime and gypsum may well be divided into two classifications for each material, namely, industrial and manufacturing. Investigations pertaining to the use in agriculture of lime and gypsum have not been considered within the scope of this chapter with the exception of those which are also applicable to other uses. Furthermore, no effort has been made to cover completely those uses such as the treatment of sewage, the manufacture of heavy acids, etc., in which lime or gypsum is at present the subject of much study and which are reviewed in more detail in other chapters.

Lime, Industrial. The industrial uses of lime in the United States are quite numerous. Consequently a relatively large percentage of the investigative work on lime has had a bearing in this direction.

Rogers [1] reports the composition of thirty-five chemical limes (hydrates and quicklimes) from various sections and discusses the limits with respect especially to minor constituents, which might be imposed without undue hardship.

Hooker [2] suggests the quality of lime best suited for the absorption of chlorine in paper mill "bleach-liquor" practice and gives a method for evaluating hydrated lime for this purpose.

Arthur [3] discusses quicklime *vs.* limestone in the manufacture of glass and indicates the desirable properties of lime for this purpose.

Pierce, Setzer and Peter [4] developed a titrometric method for the determination of calcium and magnesium carbonates in lime-

[1] Rogers, *Ind. Eng. Chem.,* **19**: 1157 (1927).
[2] Hooker, *Ind. Eng. Chem.,* **19**: 712 (1927).
[3] Arthur, *Ind. Eng. Chem.,* **19**: 711 (1927).
[4] Pierce, Setzer and Peter, *Ind. Eng. Chem.,* **20**: 436 (1928).

stone. Shaw, MacIntire and Underwood[5] compared the modified Scaife and sucrose methods of determination of "available" lime or "causticity." They also propose two modifications in procedure and filtration devices to secure more concordant results.

Shaw and MacIntire[6] studied the influence of certain impurities upon the "causticity" of limes as determined by the modified Scaife and sucrose methods, with certain changes.

Lime, Manufacture. Ray and Mathers[7] determined the effect of the time and temperature of burning upon the properties of a high calcium quicklime and hydrate made therefrom. Linzell, Holmes and Withrow[8] studied the loss in weight of limestone as a function of time and temperature of burning. They found that the maximum loss in weight varies with the composition of the stone and that the rate of decomposition is also a function of the composition; furthermore, that the minimum temperature of burning depends upon the partial pressure of the carbon dioxide present.

Azbe[9] shows by graphs the loss and reabsorption of carbon dioxide by limestone and failure of magnesium oxide to reabsorb carbon dioxide even in an atmosphere rich in CO_2. This same investigator also shows[10] that the introduction of steam into a lime kiln is not beneficial in so far as calcination is concerned, as it is usually wasteful of fuel and may cause local high temperatures although it does reduce the average temperature. Azbe claims, however, that the use of steam may sometimes be justified to prevent clinkering in gas producers.

Haslam and Smith[11] report a rather comprehensive study of the flow of heat through limestone with and without dissociation and give some curves from which it is possible to determine the time necessary for complete dissociation of various sizes of pieces of stone under different conditions of preheat and with different surface temperatures.

Several patents for the manufacture of plastic hydrated lime were granted during the year. Dittlinger's[12] is based upon the addition of certain substances to the hydrating water. Hunter[13]

[5] Shaw, MacIntire and Underwood, *Ind. Eng. Chem.*, **20**: 312 (1928).
[6] Shaw and MacIntire, *Ind. Eng. Chem.*, **20**: 315 (1928).
[7] Ray and Mathers, *Ind. Eng. Chem.*, **20**: 415 (1928).
[8] Linzell, Holmes and Withrow, *Trans. Am. Inst. Chem. Eng.*, 18: 249 (1926).
[9] Azbe, *Rock Products*, **30**. no. 16: 54 (1927).
[10] Azbe, *Rock Products*, **30**, no. 7: 63 (1927).
[11] Haslam and Smith, *Ind. Eng. Chem.*, **20**: 170 (1928).
[12] Dittlinger, U.S.P. 1640602 (Aug. 30, 1927).
[13] Hunter, U.S.P. 1634424 (July 5, 1927).

discharges the hot quicklime direct from the kiln into an excess of water and then dries the hydrate. Carson [14] reduces the quicklime to finer than a No. 100 screen and slakes it without permitting the temperature to exceed 100-115° C.

Gypsum, Industrial. The United States has not kept pace with other countries in the industrial uses of gypsum. Jewett and Montonna [15] attempted to determine the filtration constants for calcium carbonate and calcium sulfate and evaluate the effect of filtration variables on these constants and to compare the different equations proposed for filtration design as regards accuracy and adaptability. The constants m, n, and K of Lewis and Almy's equation were determined under varying conditions of pressure, concentration of sludge, viscosity and surface tension of filtrate.

Jackman [16] reports the use of gypsum in place of sulfuric acid on a laboratory scale for the recovery of ammonia from coal gas. He describes two different methods, one direct, the other indirect.

Gypsum, Manufacture. Brookby [17] patented a light weight cellular gypsum product, formed by the contraction of calcium caseinate in drying, the caseinate being added to the slurry. It is claimed that this product is suitable for use in the manufacture of plaster and wall board.

Farnsworth [18] reports a study by X-rays of discarded plaster molds and states that the addition of 0.25% Al_2O_3 before calcination results in a product quite satisfactory as regards strength. Murray [19] at the Bureau of Standards studied the effect of (a) amount of mixing water, (b) retardation, (c) humidity, (d) amount of sand, (e) grading of sand, (f) grading of plaster, (g) method of calcination and (h) admixtures on the expansion on setting of a calcined gypsum.

[14] Carson, U.S.P. 1613341 (Jan. 4. 1927).
[15] Jewett and Montonna, *Chem. Met. Eng.*, **34**: 86 (1927).
[16] Jackman, *Gas J.*, **175**: 428 (1926).
[17] Brookby, U.S.P. 1638001 (Aug. 2, 1927).
[18] Farnsworth, *Ind. Eng. Chem.*, **19**: 714 (1927).
[19] Murray, *Rock Products*, **31**, no. 2: 88 (1928).

Chapter XXXV.

Clay Products.

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Clays. The greatest interest on the part of ceramists neces-sarily centers upon the chemical and physical properties of the many types of clay. For this reason the very complete study of 13 plastic ball clays and 7 kaolins made by Parmelee and McVay [1] of the University of Illinois is of considerable interest to the industries. A great mass of information is presented.

In this connection there should be mentioned also the Bureau of Standards Circular No. 325 (1927), which concerns itself with the properties of American white burning clays.

Industrialists are much interested in the clays employed in the making of kiln furniture, the life of which has a good deal to do with the returns of a plant. The Bureau of Standards has made a third progress report on this subject, reported by Heindl and Pendergast. [2] This work dealt principally with the modulus of elasticity and the transverse strength of clay bars, at several tem-peratures. It is suggested that the expression: $R = M/Ec$, where R = relative resistance of the clay, M = modulus of rupture, E = modulus of elasticity, and c = coefficient of linear thermal expan-sion, may assist in evaluating the suitability of a clay for the making of kiln refractories.

The broad subject of the plasticity of clay and its measurement was studied by Talwalkar and Parmelee [3] in which they first discussed the various methods suggested for this purpose and finally adopted the method of subjecting the clay specimen to torsion. They subjected cylinders of plastic clay, one inch in diameter and four inches long, to a torsional stress and obtained

[1] Parmelee and McVay, *J. Am. Ceram. Soc.*, **10**: 598 (1927).
[2] Heindl and Pendergast, *J. Am. Ceram. Soc.*, **10**: 524 (1927).
[3] Talwalkar and Parmelee, *J. Am. Ceram. Soc.*, **10**: 670 (1927).

the stress-strain diagram. The load which produces torsion is plotted against the deformation in degrees. The plasticity index is taken to be the total deformation at the point of failure, divided by the average stress beyond the proportional limit. The results obtained are not entirely convincing.

The plasticity of clays was also made the subject of a study by Jenks,[4] who seeks the cause of this property in the formation of a gelatinous envelope surrounding the non-gelatinous particles. The time honored slaking test (under a new name) is used as the criterion of plasticity. The effect of LiCl on increasing the slaking time was studied. It was found that a combination of NaOH and NaCl produced similar results.

The plasticity and working property of clay from the practical standpoint has received consideration by McDowell.[5] He suggests the method of applying a load of 8000 grams to a two inch cube of plastic clay and noting the deformation produced after 30 seconds. Sufficient water is to be added to a clay to produce normal deformation, equivalent to normal workability. The proper deformation of a terra cotta body was found to lie between 0.625 and 0.813 inch for a two inch cube and the standard load.

The air occluded by clay in the plastic and the suspended states is claimed by Lapp[6] to be detrimental to the formation of a sound body structure. For the purpose of producing a more perfect porcelain structure this worker subjects the body slip, previous to filter pressing, to a vacuum treatment which causes boiling of the water and the removal of the occluded air. It is claimed that the structure is actually improved, that better healing of the clay surfaces takes place, that less cracking occurs and that the material dries more easily.

A study of the hydrogen-ion concentration and the electrical conductivity of clay suspensions has been reported by Fessler and Kraner[7] in which they found that with increase in temperature the H-ion concentration decreased and the conductivity was increased. Within the limits of these experiments the conductivity increased with increase in gravity while the H-ion concentration was not changed materially. The addition of Na_2SiO_3 to the suspension decreased the H-ion concentration and increased the conductivity. $MgSO_4$ and Al_2Cl_6 increased the H-ion concen-

[4] Jenks, *J. Am. Ceram. Soc.*, **11**: 317 (1928).
[5] McDowell, *J. Am. Ceram. Soc.*, **11**: 99 (1928).
[6] Lapp, *J. Am. Ceram. Soc.*, **11**: 61 (1928).
[7] Fessler and Kraner, *J. Am. Ceram. Soc.*, **10**: 592 (1927).

tration, the conductivity and the viscosity. Conductivity measure ments could be used for the plant control of casting slips. The determination of the H-ion concentration does not appear to be as useful for plant control as the customary fluidity measurements.

A new voluminometer for the measurement of clay shrinkage has been designed by Wheeler and Kuechler ` which consists of a metal cylinder containing mercury, provided with a piston to which a burette is attached. A mercury tight contact is made by the piston. The lowering of the latter submerges the specimen and forces the displaced mercury into the burette from which the volume can be read directly.

A study of brick drying on a plant scale has been conducted by Hursh[9] under the auspices of the National Brick Manufacturers Association, in which the effects of humidity, temperature and air velocity are correlated.

Feldspar. Feldspar is a most important constituent of porcelain bodies and yet the properties of the various forms of this mineral and the effect of the chemical composition upon the fusibility and fluxing power have not been clearly understood. The Bureau of Standards has undertaken the study of the feldspars used in ceramics. A second progress report has been made by Geller.[10] The tests include the determination of the fineness of the powdered, commercial mineral, the composition, temperature range of softening, thermal expansion and petrographic analysis. Furthermore, porcelain and earthenware bodies were compounded in which typical feldspars were introduced. These bodies were subjected to the usual mechanical tests. It was found that the fusibility of the feldspars as well as the softening range decrease with increase in potash content. The porosity of semi-vitreous bodies at the same firing temperature was found to be highest when feldspars of intermediate potash content were used. The thermal expansion of ceramic bodies was found to increase with increase of soda in the feldspar.

Schramm,[11] on the other hand, found that in ceramic bodies in production all feldspars produce vitrification at nearly the same temperature. The length of the firing range likewise, is very nearly the same, and a 7% potash feldspar over-fires together with one containing 13% K_2O.

[8] Wheeler and Kuechler, *J. Am. Ceram. Soc.*, **10**: 807 (1927).
[9] Hursh, Rept. 2 and 3, Research Committee, National Brick Manufacturers Association, 1927-1928.
[10] Geller, *J. Am. Ceram. Soc.*, **10**: 411 (1927).
[11] Schramm, *J. Am. Ceram. Soc.*, **10**: 1005 (1927).

During the latter part of 1927 the Bureau of Standards [12] re- ported additional results dealing with the comparative fluxing effect of potash and soda feldspars. The interesting statement was made that all bodies containing feldspar high in potash showed the smallest thermal expansion at 700° and that the expansion seems to increase with the soda content. The same laboratory measured the linear thermal expansion of typical feldspars, be- tween room temperature and 560° and found it to be between 0.402 and 0.542% for feldspars fired to cone 8, between 0.387 to 0.594 when fired at cone 10, 0.404 to 0.473 when fired at cone 12, and 0.401 to 0.450 when fired at cone 14.

In all reactions between solids the particle size is of paramount importance. This holds especially for the ground feldspar and quartz in ceramic bodies. A number of determinations of the fineness were made by the sedimentation method by Schramm and Scripture [13] upon commercial feldspars and flints. The results ob- tained brought out the fact that the batch ground materials showed a greater average fineness than those ground in continuous mills. This difference can be overcome by using a slightly larger amount of the coarser minerals. Incidentally, it was shown that the cus- tomary sieve tests are of no value for indicating the real fineness of any mill product.

Heat Effects upon Clays and Ceramic Bodies. A con- venient, though rather expensive, platinum wound resistance furnace, provided with end coils and a chromel-alumel booster coil, suitable for precision laboratory work in ceramic studies was described by Orton and Krehbiel. [14]

Further work upon the thermal reactions of clays has been reported by MacGee. [15] The endothermic reaction at 550° absorbs from 40 to 130 cals per gram of dried material. The exothermic reaction at 950° evolves from 5 to 30 cals per gram of dry sub- stance. Through the interval, 20 to 1100°, the specific heat of practically all clays lies between 0.4 to 0.5, but the specific heat between 20 to 100° varies only from 0.2 to 0.3. The fuel require- ment for a given mass of clay depends not only upon the specific heat but also upon the thermal conductivity and the specific gravity.

[12] *Ceram. Ind.,* **9:** 390 (1927); Bureau of Standards, Tech. News Bull., no. 129 (1928).
[13] Schramm and Scripture, *J. Am. Ceram. Soc.,* **10:** 264 (1927).
[14] Orton and Krehbiel, *J. Am. Ceram. Soc.,* **10:** 373 (1927).
[15] MacGee, *J. Am. Ceram. Soc.,* **10:** 561 (1927); Ohio State Univ., Eng. Series. Bull. no. 38.

A very complete study of the heat balance of ceramic kilns in general and of one downdraft and three Hoffmann continuous kilns was reported by Baumann.[16]

The heat required to fire ceramic bodies has been studied also by Simpson [17] both with reference to laboratory measurements and operating kilns. It was found that the interval specific heat for fire clays, shales and surface clays varied between 0.425 to 0.440 and that the average kiln efficiencies were about 29%.

The effect of temperature on the optical properties of kaolinite was determined by McVay.[18] Euhedral crystals of kaolin became uniaxial negative at 625° (the metanacrite of Rinne) and retained this form until 1400° was reached. At 1450° the crystallization of mullite and the formation of glass were noted.

A study of the dehydration and firing behavior of clays was carried on at the Bureau of Standards and reported by Geller and Wadleigh.[19] It was found that fire clays were more difficult to dry than shales and surface clays. It appears possible that clay products may be fired to 1830° F. in 20 hours.

The microstructure of white earthenware bodies fired to different temperatures was studied by Insley.[20] He found that mullite crystals are formed at comparatively low temperatures, that the size of the crystals increased with the temperature and that there seemed to be a distinct relation between the development of mullite within the body and the crystal growth extending out into the glaze.

While it is assumed that ceramic bodies become relatively inert to chemical solvents when fired to temperatures above 1200° it was found by Bleininger [21] that this is not necessarily true. Upon treating pulverized samples of earthenware with hot H_2SO_4, it was possible to extract as much as 66% of the anhydrous clay present in the body when the absorption was 18%. It appeared that for well matured bodies a minimum permissible solubility should exist and that the acid treatment could be used to trace the development of the acid insoluble condition.

A very interesting aspect of the progressive maturing of ceramic bodies was submitted by Orton and Krehbiel.[22] When the firing

[16] Baumann, *J. Am. Ceram. Soc.,* **10**: 860 (1927).
[17] Simpson, *J. Am. Ceram. Soc.,* **10**: 897 (1927); Ohio State Univ., Eng. Series, Bull. no. 38.
[18] McVay, *J. Am. Ceram. Soc.,* **11**: 224 (1928).
[19] Geller and Wadleigh, *J. Am. Ceram. Soc.,* **10**: 925 (1927).
[20] Insley, *J. Am. Ceram. Soc.,* **10**: 317 (1927).
[21] Bleininger, *J. Am. Ceram. Soc.,* **10**: 535 (1927).
[22] Orton and Krehbiel, *J. Am. Ceram. Soc.,* **11**: 215 (1928).

process of ceramic bodies is interrupted by chilling or the temperature is held stationary too long, freezing takes place. This means that the body so treated becomes refractory at this point and cannot be brought forward in the normal way without the use of a considerably higher temperature. The authors considered this phenomenon from the standpoint of the pyrometric cones so generally used in the clay industries. They found that different feldspars may be important factors in this connection. Thus, a Swedish feldspar showed this tendency much less than some American minerals. The influence of feldspar appeared to be very real but other factors seem to be involved as well. These have not yet been differentiated.

Glazes. The problem of glaze fit governing the attachment of the glasses, used as glazes, to the clay bodies was made the subject of an extensive study by the Bureau of Standards,[23] which has not yet been completed. The work consists in the determination of the tensile strength, modulus of rupture and the thermal expansion of the various types of glazes. The expansion measurements have been made by the Fizeau-Pulfrich method with the use of the interferometer. The expansion-temperature curves are not strictly linear as the slope increases slightly with the temperature. The mean coefficient of linear expansion has been found to vary from 0.0456×10^{-4} to 0.1581×10^{-4}. The former value is for high magnesium glass, the latter for a high potash-soda glass. It is expected that ultimately the expansion values for the individual oxides will be evaluated.

Glazes frequently crack or craze after the products have stood or have been in use for some time. This delayed type of failure has been studied by Schurecht[24] and has been found to be due to an after-expansion which takes place most markedly on porous bodies which are appreciably soluble in H_2SO_4. It would seem that there might be an absorption of water either chemically or physically which causes this increase in volume. This assumption is supported by the fact that materials prone to show such crazing show a loss in weight when heated above $110°$. The author suggests an autoclave test for determining the tendency to develop delayed crazing. A steam pressure of from 150 to 175 lbs. per sq. in., maintained for one hour is suggested.

A study of terra cotta slips which are dense but not glassy

[23] Bureau of Standards, *Tech. News Bull.* no. 128 (1927).
[24] Schurecht, *J. Am. Ceram. Soc.,* 11: 271 (1928).

coatings applied to the surface of terra cotta has been made by Hill.[25] The safest composition seems to be one consisting of 43.75% clay and 56.25% of equal amounts of Cornwall stone and feldspar. Crazing of the slip may be reduced by increasing the clay content, substituting Cornwall stone for feldspar and china clay for ball clay. Cracking is overcome by increasing the Cornwall stone and substituting china clay for ball clay.

Properties of Ceramic Bodies. The physical properties of chemical stone ware were determined by MacGee.[26] The compressive, transverse and impact resistance as well as the thermal expansion and elasticity of chemical stoneware bodies were determined. The ordinary semivitreous stoneware body expands about 0.3% when heated from room temperature to 500°. The crushing strength varies from 10,000 to 26,000 lbs. per sq. in. The transverse strength is from 1600 to 2800 lbs. per sq. in. for bars broken on a five inch span. The modulus of elasticity varies from 10×10^5 to 18×10^5, measured on a five inch span. Stoneware bodies will lose about 75% of their impact resistance when subjected to 10 alternate heatings and coolings, from 400 to 30°.

The impact and static transverse strength of wet process electrical porcelain was determined by Navias.[27] For the impact test the Charpy machine was used. The average value for specimens 0.5 inch in diameter was 1.24 ft.-lbs. per sq. in.; for 0.75, 1 and 1.125 inch cylinders it was 1.53 ft.-lbs. per sq. in. The average modulus of rupture was found to be 11,000 lbs. per sq. in.

Bricks were tested for tensile strength by McBurney.[28] A self-aligning grip was used. The mean tensile strength varied from 210 to 601 lbs. per sq. in. These values are between 30 to 40% of the modulus of rupture.

The properties of the refractories used in zinc metallurgy have been examined by Wheeler and Kuechler,[29] who submit a large amount of test data.

The physical properties of artificial aluminous abrasives were determined by Purdy and MacGee [30] in a very comprehensive investigation. There were determined the compressive strength, expressed in lbs. per sq. in., the porosity in %, the modulus of rupture in lbs. per sq. in., the modulus of elasticity in lbs. per sq.

[25] Hill, *J. Am. Ceram. Soc.*, **11**: 260 (1928).
[26] MacGee, *J. Am. Ceram. Soc.*, **10**: 569 (1927).
[27] Navias, *J. Am. Ceram. Soc.*, **10**: 90 (1927).
[28] McBurney, *J. Am. Ceram. Soc.*, **11**: 114 (1928).
[29] Wheeler and Kuechler, *J. Am. Ceram. Soc.*, **10**: 109 (1927).
[30] Purdy and MacGee, *J. Am. Ceram. Soc.*, **11**: 192 (1928).

in., the resistance to impact in gram-cm. per sec.,[2] the mechanical endurance in number of blows, the thermal expansion between 30-724° and the resistance to heat shock after 10 quenchings from 400° expressed in per cent of the original resistance to impact. The results are compiled in the following table:

	Very Soft	Medium Soft	Medium	Hard
Grade	81	60	41	19
Porosity	30	28	25	24
Specific gravity	3.85	3.77	3.67	3.43
Modulus of rupture.....	1500	1700	2300	2600
Impact strength	1.86×10^{6}	2.35×10^{6}	3.14×10^{6}	3.42×10^{6}
Heat shock resistance ...	78	73	68	62
Mechanical endurance ..	1510	1650	2800	4930
Crushing strength	5200	6100	8100	11300
Modulus of elasticity....	4.1×10^{5}	6.2×10^{5}	6.9×10^{5}	6.6×10^{5}
Coefficient of thermal expansion	7.7×10^{-6}	......	7.7×10^{-6}	7.4×10^{-6}

Special Products. Westman[31] replaced the ground quartz used in porcelain bodies by ground fused quartz, suggesting the name of fusilain for the new product. A comparison was made between a regular electrical porcelain body and one of the same composition but containing fused quartz. It was found that the quartz glass body developed a vesicular structure unless slightly reducing kiln conditions were maintained, and it matured about 60 to 80° below the maturing point of the regular body. A very dense product was obtained. The thermal expansion of the quartz glass body was much lower than that of the regular body and more steady.

A talc porcelain used in the German Bosch spark plug was analyzed and found to contain: SiO_2, 66.43; Fe_2O_3, 2.11; Al_2O_3, 3.72; MgO, 27.78; K_2O, 0.02; Na_2O, 0.02; loss on ignition, 0.11%. A body consisting of 80 calcined talc and 10 to 15 of clay substance seemed to be the best composition.[32]

Aluminous refractories obtained through the introduction of cyanite and diaspor in clay refractories were studied by Vachuska and Bole[33] and a large number of test results are submitted.

The properties of special porcelains containing varying amounts of calcined cyanite were made the subject of an investigation by McDowell and Vachuska.[34] These porcelains were fired at tem-

[31] Westman, *J. Am. Ceram. Soc.*, **11**: 82 (1928).
[32] *Ceram. Ind.*, **10**: 152 (1928).
[33] Vachuska and Bole, *J. Am. Ceram. Soc.*, **10**: 761 (1927).
[34] McDowell and Vachuska, *J. Am. Ceram. Soc.*, **10**: 64 (1927).

Chapter XXXVI.

Coal, Coke and By-Products (Not including Gas).

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Progress in America on the chemistry of coal, coke and by-products as measured by the number of contributions to the literature is again far behind that of European nations. A review of the sources of the papers abstracted in the Fuels Section of Chemical Abstracts shows the United States far in the rear of Germany, England and France, both on the basis of number of papers per capita population and per ton of coal mined. Doubtless this condition is due to the lack of financial support for coal research. Neither the Government nor private industry has yet appreciated the importance, from a national point of view, of sup porting a progressive program of fundamental research on coal and coal processing. However, it is hoped that the growing interest in fuel problems, as evidenced by the activities of the fuel committees and divisions of professional societies and industrial associations, will crystallize ultimately in the adequate support of research in the fuel field. The Second International Conference on Bituminous Coal to be held at the Carnegie Institute of Tech nology in November, 1928, promises to be even more successful in this respect than the Conference of 1926.

The Classification of Coal. Early in 1927, a sectional committee on the classification of coal was organized by the American Engineering Standards Committee to study systems of classifying coal and, if possible, to work out a unified system of scientific

classification of American coals, as well as another system based on use of coal. This committee is now fully organized and at work on collecting data on the composition, constitution and use of American and Canadian coals. At the annual meeting of the American Institute of Mining and Metallurgical Engineers, held in New York in February, 1928, a symposium on coal classification was held, at which a series of papers on various aspects of coal classification were presented. Seyler,[1] of England, described his method of classifying coal on the basis of ultimate analysis and discussed the relation between systems based on ultimate and proximate analyses. Rose[2] presented the Ralston triangular diagram, in which the percentages of carbon, hydrogen, and oxygen of a large number of coals were plotted. He showed that coking and other properties of coal could be predicted to a considerable degree from the position of the coal on the diagram. Tideswell and Wheeler[3] also favored using the ultimate analysis as a basis of classification and pointed out the desirability of eliminating or correcting for the errors in the ultimate analysis due to carbonates, pyrites and shaley matter in the coal. Classification based on proximate analyses as used by the U. S. Geological Survey and the slacking characteristics of low-rank bituminous coals and lignites were discussed by Campbell,[4] and Parr's method of classifying by the per cent volatile matter and calorific value of the dry ash-free coal was described by Fieldner.[5] Francis[6] advocated a new method based on the relative oxidizability of the coal "ulmins" by dilute nitric acid. He showed a fairly definite relation between the rank of a coal and the amount of alkali soluble "ulmins" produced by an oxidation at 150° C. or accelerated oxidation with chemical oxidizing agents such as dilute nitric acid and potassium chlorate.

Constitution and Origin of Coal. Coöperative research on the constitution of coal conducted jointly by the U. S. Bureau of Mines and the Safety in Mines Research Board of England has been continued during the year, with special reference to a

[1] Seyler, "The classification of coals." Presented at New York meeting, Am. Inst. Mining Met. Eng., Feb., 1928.
[2] Rose, Discussion at New York meeting. Am. Inst. Mining Met. Eng., Feb., 1928.
[3] Tideswell and Wheeler, Am. Inst. Mining Met. Eng., *Tech. Pub.* no. 104 (1928). 12 p.
[4] Campbell, Discussion at New York meeting, Am. Inst. Mining Met. Eng., Feb., 1928.
[5] Fieldner, Discussion at New York meeting, Am. Inst. Mining Met. Eng., Feb., 1928.
[6] Francis, "The classification of coal in the light of recent discoveries with regard to the constitution of coal." Presented at New York meeting, Am. Inst. Mining Met. Eng., Feb., 1928.

study of the coal "ulmins" in British and American coals. Francis and Wheeler [7] find that the "ulmic" (or "humic") matter, which comprises 70 to 95% of most coals, is converted into a form soluble in alkali by slow oxidation with air at low temperatures (150° C.) and that the rate at which this conversion takes place is indicative of the rank of the coal. Low-rank coals such as lignites or sub-bituminous oxidize much faster than high-rank bituminous coal. According to Francis,[8] these readily oxidizable "ulmins" are responsible for the spontaneous combustion of coal. Turner and Sinkinson [9] also have contributed a paper giving data on the heat evolved by coal during the absorption of carbon dioxide. They consider that the rate at which coal absorbs CO_2 "is an important factor in the production of the initial temperatures necessary for its spontaneous combustion." The effect of pressure and temperature factors on the progressive metamorphism of coals from lower to higher rank was discussed by White before the National Academy of Sciences. He concludes that "the factor of preëminent importance in the metamorphism of coal and other sediments on a regional scale, independent of igneous influences which, in general, are merely local, is horizontal thrust. Vertical pressure . . . due to the thickness of overlying rock is relatively insignificant."

Clinkering of Coal Ash. Research on coal ash fusibility and clinkering in furnaces has continued throughout the past year at the Pittsburgh Experiment Station of the Bureau of Mines. Tests on 21 coals, ranging in ash fusibility from 1990 to 2930° F. lead to the following conclusions : [10] 1. The quantity of clinker formed decreases as the rate of burning increases, although the density and fusion of the clinker pieces are greater at the higher rates. 2. The quantity of clinker formation has a fairly definite relation to the softening temperature of the coal ash. It decreases with increase of temperature. 3. This relation is better expressed by using the softening temperature than it is by that of the initial or fluid temperatures. 4. The relation becomes more consistent as the size of the coal decreases. The influence of size of coal pieces on the quantity of large clinkers is greater as the large pieces of extraneous matter are more refractory, and are not maintained at their fusion temperatures sufficiently long to slag completely.

[7] Francis and Wheeler, *J. Chem. Soc.*, 1927: 2958.
[8] Francis, Am. Gas Assoc., Preprint, 1927. 6 p.
[9] Turner and Sinkinson, *Pulp Paper Mag. Can.*, **25**: 681 (1927).
[10] Fieldner, Selvig and Nicols, *Trans. Am. Soc. Mech. Eng.*, **50**: 33 (1928).

In a plant study of the action of coal ash on boiler furnace refractories, Sherman and Taylor,[11] of the Bureau of Mines, found that the composition of the coal ash fired in the furnace and that picked up by the gases and deposited on the furnace walls differed. In general, the ash suspended in the furnace gases contained more iron oxide than the average ash and was of more fusible nature. Low-fusion ashes produced erosion of the fire-brick furnace walls.

Analyses of American and Canadian Coals. Within the past year the Bureau of Mines has issued technical papers containing analyses of "mine" samples and "delivery" samples of Oklahoma, Arkansas, Indiana and West Virginia coals.[12]

The Canadian Department of Mines [13] also has published a bulletin containing 230 analyses of Canadian, British and American coals delivered to government buildings.

Methods of Sampling and Analysis of Coal. Committee D-5 [14] on Coal and Coke, of the American Society for Testing Materials has proposed tentative methods for determining cubic foot weights of coke and crushed bituminous coal and for making sieve analysis of the same materials. Kohout [15] verified experimentally the earlier work of Register which showed that gaseous nitrogen is essential in the atmosphere of a bomb calorimeter to completely oxidize sulfur to sulfur trioxide. The oxides of nitrogen function catalytically. With nitrogen present, sulfur in fuels may be determined accurately with the bomb calorimeter. Carr and Rente [16] and also Watkins [17] have published modifications for using the bomb calorimeter in determining total carbon in coal.

Coal Preparation. Highly competitive conditions in the bituminous coal industry have forced better methods for cleaning and preparing coal. Frazer,[18] in a recent review of "Trend in bituminous coal preparation," describes several new methods for washing and dewatering coal and Campbell [19] has summarized the present status of various wet and dry cleaning methods with a brief exposition of the principles underlying each method and its application to various types of coal. On the scientific side of coal

[11] Sherman and Taylor, *Mech. Eng.*, **49**: 735 (1927).
[12] Bur. Mines, Tech. Papers 405, 411, 416, 417.
[13] Nicolls, Can. Dept. Mines, *Investigations of Fuels and Fuel Testing*, no. 671: 106 (1927).
[14] *Proc. Am. Soc. Testing Materials*, **27**, pt. I: 492 (1927).
[15] Kohout, *Ind. Eng. Chem.*, **19**: 1065 (1927).
[16] Carr and Rente, *Ind. Eng. Chem.*, **20**: 548 (1928).
[17] Watkins, *Ind. Eng. Chem.*, **19**: 1052 (1927).
[18] Frazer, *Coal Mining*, **5**: 119 (1928).
[19] Campbell, Am. Inst. Mining Met. Eng., *Tech. Pub.* no. 117 (1928), 31 p.

washing, Bird and Yancey [20] of the Bureau of Mines have made a fundamental study of the action of coal washing tables and the application of hindered settling classification to the table feed or to retreating middlings.

Agglutinating Value or Coking Power of Coal. One of the common methods for determining the agglutinating or coking power of a coal consists in determining the maximum weight of inert matter (sand or powdered carbon) that can be mixed with a given weight of pulverized coal and yet obtain a coherent lump of coke on heating. Fulweiler and Cleveland applied the Barash method for making this test to a series of American coals and obtained ratios for coking coals varying between limits of 1 : 1 to 26 : 1. Coffman and Layng [21] propose the use of the Layng-Hathorne plastic temperature test for evaluating the agglutinating power of coal and have published data showing that this agglutinating index is a measure of coking properties and shows the effect of weathering [22] and oxidation on the coking properties of a coal. A temperature of 150° C. in air seems to be the maximum to which a coal can be heated without it being detrimental to its coking properties, while preheating may be carried on to higher temperatures in an inert atmosphere without affecting the nature of the coke formed.

There is need for further work in standardizing a method for determining agglutinating value and then this test should be applied to coals of known behavior in coke ovens, gas retorts and producers to correlate the indications of the test with the behavior of coals in practice.

Coke. The physical and chemical properties of coke in relation to industrial and domestic use continues to be of interest to both producers and consumers. Gilmore, Mohr and others [23] of the Canadian Department of Mines have made a comprehensive examination of typical cokes sold in Canada as household fuels. The terms "combustibility" and "reactivity" as applied to coke have been the subjects of much discussion and experimentation in both Europe and America during recent years. The terms have been used rather loosely, but practice is now tending toward restricting "combustibility" to the rate of combining with oxygen,

[20] Bird and Yancey, Am. Inst. Mining Met. Eng., *Tech. Pub.* no. 76 (1928), 22 p. *Tech. Pub.* no. 77 (1928). 11 p.
[21] Coffman and Layng, *Ind. Eng. Chem.*, **20**: 165 (1928).
[22] Layng and Coffman, *Ind. Eng. Chem.*, **19**: 924 (1927).
[23] Gilmore, Mohr and others, *Investigations of Fuels and Fuel Testing*, no. 671-I (1927).

and "reactivity" to rate of reaction of coke with gases other than oxygen, such as carbon dioxide and water vapor. Joseph [24] has reviewed the various concepts of the combustibility of coke as regards its behavior in the blast furnace, while Fieldner and Davis [25] have covered the same subject with respect to coke for the foundry cupola. In conducting laboratory tests on the reactivity of coke with carbon dioxide or water vapor, Davis and Reynolds [26] found that the duller portions of the same piece of coke were more reactive than the bright lustrous parts, and that the reactivity increased with the absorptive capacity of the coke for carbon dioxide. Parr and Staley [27] believe that the ignition temperature of coke in air is a measure of its "reactivity." Reactive cokes have relatively low ignition temperatures. Their method consists of heating the coke samples at slowly increasing temperatures in a constant stream of oxygen. The crossing point of the temperature curves of the coke and the electric furnace is taken as the "ignition" or "critical temperature."

The rate of reaction of coke with air is much faster than carbon dioxide. Ward and Hamblen [28] heated a carbon block and withdrew samples from its center. Analyses of these showed a greater concentration of oxygen as CO_2 on the carbon side of the enveloping gas film than on the air side as free oxygen. This is what would be expected from the inverse square diffusion law if the rate of combustion of carbon were limited only by the rate of diffusion of oxygen through the gas film. Hence, when solid carbon burns in air the rate of chemical interaction of carbon and oxygen is not the controlling factor but rather the rate of diffusion of the combustion gas through the gas film.

The mechanism of the steam-carbon reaction has also received attention at the Massachusetts Institute of Technology. Thiele and Haslem,[29] working with steam activated vegetable charcoal, arc-electrode carbon, a natural graphite and retort carbon, found that the type of carbon greatly affected the mechanism, in degree at least, of the reaction. With these very different kinds of carbon, the reaction with steam behaves as if it were of the "zero" order, with respect to changes in the partial pressure of the steam. With

[24] Joseph, *Am. Iron Steel Inst.*, Advance paper, Oct. 28, 1927. 24 p.
[25] Fieldner and Davis, *Fuels and Furnaces*, **5**: 1181 (1927).
[26] Davis and Reynolds, *Ind. Eng. Chem.*, **20**: 617 (1928).
[27] Parr and Staley, *Ind. Eng. Chem.*, **19**: 820 (1927).
[28] Ward and Hamblen, *Ind. Eng. Chem.*, **19**: 1025 (1927).
[29] Thiele and Haslem, *Ind. Eng. Chem.*, **19**: 882 (1927).

retort carbon above 1010° C., the reaction behaves as if it were of a "negative" order. When the reaction is of the "zero" order, the pressure of the steam has little effect on the composition of the fixed gases produced; when the reaction is of a "negative" order, increase in pressure lowers the CO content of the fixed gases very much. The authors ascribe these results to the formation of a chemically combined surface layer of the C_xO_y type.

High-Temperature Carbonization of Coal. Improvement in the design of vertical retort and oven-type gas plants by American builders is continuing. A number of new installations are described in the Builders Section of the 1927 report of the Carbonization Committee of the American Gas Association.[30] The gas industry is beginning to appreciate that the processing of coal to produce gas, coke and by-products is a chemical engineering operation and Sperr and Byrne [31] have analyzed the unit operations involved. A successful plant for the recovery of phenol waste to avoid the pollution of streams is described by Jones.[32] This plant at Fairmont, West Virginia, is said to operate with an efficiency of 96%. The crude ammonia liquors are scrubbed with benzol and the benzol freed from phenol by treatment with caustic soda solution, which on acidification yields a readily marketable phenol. This is the fourth recovery plant operating in the United States.

Low-Temperature Carbonization. Strong [33] has reported the results of low-temperature carbonization tests on Westmoreland, Minto and Sidney coals. The maximum temperatures used varied from 350 to 600° C. The best yield of products was obtained at different temperatures with different coals. Carbonization at low temperatures in steam or gas gave the best tar yields.

Comparative low-temperature assay tests by the U. S. Oil Shale, Fischer (German) and Grey-King (British) methods are reported by Davis and Galloway.[34] Twenty-four coal samples were assayed for yields of oil, water, coked residue and gas. In the hands of the authors the Fischer method gave the most concordant results.

Recent developments in low-temperature carbonization in

[30] Carbonization Committee Report. New York, Am. Gas Assoc. 1927. See also *Am. Gas J.*, **127**: 45 (1927); *Chem. Met. Eng.*, **34**: 673 (1927).
[31] Sperr and Byrne, *Chem. Met. Eng.*, **35**: 22 (1928).
[32] Jones, *Chem. Met. Eng.*, **35**: 215 (1928).
[33] Strong, Can. Dept. Mines, Mines Bur., *Investigations of Fuels and Fuel Testing*, no. 671 (1927). 64 p.
[34] Davis and Galloway, *Ind. Eng. Chem.*, **20**: 612 (1928).

America have been well covered by Porter.[35] He gives the present status of the McIntyre, Parr, McEwan-Runge, Carbocite, Green-Laucks, Warner, White and Hayes processes as given, for the most part, by those in charge of their development. Opinions of members of the sub-committee as to the importance of low-temperature carbonization to the gas industry are included.

Although the commercial profits [36] to be made in low-temperature carbonization are by no means assured, yet the possibilities under special conditions of available cheap low-grade coal and prospective smokeless-fuel markets have influenced The Urbana Coke Corporation [37] to install a one-ton Russell horizontal oven with a rotary preheater to operate on the Parr process, at Urbana, Ill., and The International Combustion Engineering Corporation [38] to erect 8 rotary retorts of the German, K.S.G. type [39] at New Brunswick, N. J. This plant is expected to provide 175,000 tons of smokeless domestic fuel per year and 2.5 to 3 million cubic feet of 800 B.t.u. gas per 24 hours. The gas is to be delivered to the Public Service Corporation of New Jersey.

Aside from providing a smokeless domestic fuel, low-temperature carbonization should, according to Crawford,[40] prove an attractive proposition in conjunction with power development. Experimental work on precarbonizing powdered coal at the Lakeside plant of the Milwaukee Light and Power Co. has been under way for several years, but no definite information on the success of these experiments is yet forthcoming. Soule [41] has described the progress of this work in general terms.

Low-Temperature Tar and Light Oil. The commercial success of low-temperature carbonization is dependent to no small degree on finding more valuable uses for the tar than as fuel oil. The Bureau of Mines and private organizations have continued research on the composition of this complex mixture. Brown and Branting [42] have determined the composition of the aqueous condensate of a low-temperature tar formed in the low-temperature distillation of a non-coking Utah coal in superheated steam as follows:

[35] Porter, Carbonization Committee Report, Am. Gas Assoc., p. 49-61 (1927).
[36] Porter, *Coal Age,* **32**: 39 (1927).
[37] Montgomery, *Chem. Met. Eng.,* **34**: 668 (1927).
[38] *Gas J.,* **180**: 181 (1927).
[39] Runge, *Mech. Eng.,* **49**: 875 (1927).
[40] Crawford, *Combustion,* **17**: 94 (1927).
[41] Soule, *Combustion,* **17**: 227 (1927).
[42] Brown and Branting, *Ind. Eng. Chem.,* **20**: 392 (1928).

	Grams Per 10 Liters
Carboxylic acids	3.9
Phenols	23.0
Pyridines and ether-soluble bases	0.824
Neutral oil	1.0

The phenols found included C_6H_5OH, o-, m- and p-cresol, catechol and xylenols. Distillation yielded a resinified residue.

The proximate composition of the liquid tar was:

	Per Cent
Dust, solids, carbon	1.0
Carboxylic acids	0.25
Bases	1.7
Phenols (a) liquid	21.0
" (b) resinous	2.4
Neutral oils	66.0
Water and working loss	7.65

These groups were investigated. The phenols were C_6H_5OH, o-, m- and p-cresols, xylenols and higher homologues. The neutral oils on distilling yielded 8% to 140° C. and 65%, 140 to 275°. Half the remainder was distillable with steam. The residue contained wax, oil and resin equal to 8, 2 and 5%, respectively, of the neutral oil. Pure compounds reported from the groups were determined quantitatively and identified.

Yao Chun Cheng and Morgan [43] found that low-temperature tar acids required a higher concentration of sodium hydroxide for complete extraction than high-temperature tar acids; in the former case, 19% NaOH is sufficient, whereas in the latter 20 to 24% is required.

An interesting report [44] on the comparison of oils derived from lignite, sub-bituminous coal and from oil shale has been submitted by Horne and Bauer. Yields and properties of oils produced from 32 coals and 10 oil shales from various States are given, together with the analyses of the coals and shales. The average yields in gallons per ton were as follows: Lignites, 5; sub-bituminous coal, 12.9; bituminous coal, 30.

[43] Cheng and Morgan, *Gas Age-Record,* **59**: 737, 748, 779, 815, 851 (1927).
[44] Horne and Bauer, Bur. Mines, Reports of Investigations, Serial 2832 (1927). 34 p.

Chapter XXXVII.

Petroleum Technology and Research.

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In the following review no attempt is made to abstract or even mention by title every recent American publication dealing with petroleum technology or research, which ground is thoroughly covered by "Chemical Abstracts." On the other hand, many important technical developments are hardly mentioned in the current technical literature, and it is probably more important in such a necessarily brief review to give an impressionistic picture of the more outstanding accomplishments and current tendencies.

The consideration of future supplies of petroleum, particularly of motor fuel, by the Federal Oil Conservation Board, has probably done more to bring about earnest consideration of research than any single recent event. Industrialists are becoming more and more familiar with research that is not carried out in test tubes, which unfortunately are too often the symbol of laboratory research. The Federal Oil Conservation Board, in a report made public in January, 1928, showed that there is no substitute for petroleum gasoline available or capable of being manufactured in sufficient quantities for our needs, except at very much higher cost than the present refinery cost of gasoline. This is a very good thing for the general public and its representative legislators to know.

The report clearly indicates, however, that research is safe guarding our future, as regards oil and motor fuel. The report discusses shale oil, benzol, alcohol, low temperature carbonization of coal, and water gas reduction synthesis and the Bergius process. The estimated costs of mining oil shale, of which there is an abundance, vary from $0.40 to $2.50 per ton. It is possible that oil and motor fuel will be produced in large quantities from cheap

coal, by the Bergius process or by synthesis from water gas, before it becomes profitable to distill oil shale on a large scale in this country. The Bergius process, after a research development ex tending over more than ten years, is now being operated on an industrial scale in Germany and its operation is being steadily increased. Its operation in America can hardly be profitable so long as petroleum is produced here in anything like its present abundance. However it should be noted that, operating on German coals, the Bergius process yields 93 to 133 gallons of crude oil per ton of coal, of which crude oil about 40 gallons is suitable for use as motor fuel. One naturally compares the Bergius process with cracking processes. The Bergius process uses hydrogen at pressures of 2100 to 3000 lbs. at 800 to 900° F. Up to the present the process is a batch process carried out in apparatus of relatively small capacity. American oil cracking units of the best modern type, operating continuously on fuel oil or heavy charging stock distillate, put through 3000 bbls. or more raw oil charging stock per day at 200 to 250 lbs. pressure, producing about 40% gasoline. One well-known process operating at about 600 lbs. pressure has units in operation having a daily through put of over 5500 bbls. and a gasoline yield of about 35%. These gasoline yields become 65-70% when residual oils are re-cycled. It is difficult, therefore, to see how the Bergius process can compete in this country with modern cracking processes at anything like present oil and gasoline price levels. However, the mechanical technique of the Bergius process is probably no more difficult than that of ammonia syn thesis, which has been highly perfected by American engineers and using American special steels.

The research on the water gas synthesis of motor fuel has also been carried out mainly in the European laboratories of Fischer and Patart. Smith, Davis and Reynolds [1] state that, with a catalyst consisting of metallic cobalt, manganese oxide and a small proportion of copper, about 1400 cubic feet of water gas was required to produce a gallon of liquid oil. At a cost of 20 cents per M. for water gas this is a material cost of 28 cents per gallon of oil, or about four times the average refinery cost of finished gasoline over the past year. Fischer has reported yields which on the same basis would correspond to a material cost of about 20 cents per gallon of oil. One of the interesting products of the Fischer process is

[1] Smith, Davis and Reynolds, *Ind. Eng. Chem.*, 20: 462 (1928).

high melting paraffin wax. Francis,[2] from thermodynamic considerations, states that the synthesis of paraffins from water gas can take place only below about 450° C.

Everyone does not have the same thing in mind when speaking of research. It is when research coöperates fully with engineering that the greatest industrial results are obtained. It is this aspect of recent progress in petroleum technology which should be most gratifying to all who believe in a scientific basis of technology. Better engineering continues to reduce labor costs, fuel costs and depreciation. Mills has recently described the operation of the Richfield refinery near Los Angeles, which runs about 45,000 bbls. of crude per day with a total force, including the refinery office, of less than 100 men, most of these men working in eight hour shifts. The cracking plant, consisting of four Cross units, is operated by one superintendent and thirteen operators.

The more efficient modern equipment of the best refineries is built by or with the assistance of engineering and equipment concerns employing competent specialists, to a much greater degree than heretofore. This factor together with considerable exchange of technical information, publication of better engineering data and courtesy plant inspections, has certainly done a great deal to speed up the technical advance of nearly the whole industry. The following notes will illustrate these facts.

Plant Technology. The anti-knock value of motor fuels continues to be much discussed and great advances have been made in producing cracked gasolines of high anti-knock values of such quality that the addition of special anti-detonating agents is, in many cases, not necessary. To a limited extent this has been accomplished by the selection of certain crudes, such as California, Smackover, Spindle Top and Mirando crude. The reason for the high anti-knock value of cracked gasolines made from these oils obviously lies in the character of the hydrocarbons, but practically nothing is known as to this, beyond the general fact that all of the crudes mentioned are of the naphthenic type. The Mirando crude is indeed quite remarkable in yielding a cracked gasoline by pressure distillation which is fully equal to benzene in anti-knock properties. This crude is also quite remarkable in giving lubricating oil distillates of exceptionally high viscosity for a given boiling point.

[2] Francis, *Ind. Eng. Chem.*, **20**: 277 (1928). Francis has also derived equations for the free energies of formation of methane, ethane, octane, acetylene, ethylene, benzene and cyclohexane, as functions of temperature.

Great advance has also been made in improving anti-knock values of cracked gasolines from light paraffin type crudes. One plant of the pressure type is producing a cracked gasoline from the gas oil from a light paraffin base crude, which is equal to commercial premium anti-knock gasoline. This change in the character of the cracked gasoline produced has been effected chiefly by increasing the cracking temperatures employed. It is possible, from the results so far obtained, that the special manufacture of blending material, such as vapor phase gasoline, will not be necessary. The daily capacity of the standard pressure distillation processes has been considerably increased; for example several units rated at 2000 bbls. daily throughput, when installed about two years ago, are now putting through 5700 bbls. per day and obtaining the same gasoline yield as was obtained at the 2000 bbl. rate.

The high anti-knock value of gasoline made by cracking in the vapor phase has long been known. It will be recalled that vapor phase processes were tried out commercially many years ago and it was definitely proven that the cost of manufacturing gasoline, by all of the processes operating in this way, was greater than for gasoline produced by pressure distillation. In spite of this fact, and in spite of the great improvement in pressure distillation processes, interest in vapor phase cracking has been revived in the general search for motor fuel of high anti-knock value. Up to the present, most of the vapor phase cracking plants which have been installed have been relatively small and are generally regarded as being experimental. Probably owing to the widespread idea that this type of cracking is a wide open field with respect to patents, and owing to the great emphasis which has been put upon anti-knock motor fuels and particularly to the fact that almost any method of passing oil vapors through a hot tube will give more or less cracked gasoline, a large number of so-called processes are being exploited. In the exploitation of such processes, special features are sometimes emphasized, sometimes patented, which have little or nothing to do with the results. De Florez,[3] well known for his work in this field, has described vapor phase cracking and pointed out that the chief operating problem to be contended with is that of efficient heat transfer. It is not sufficient to have a uniformly heated surface but some provision must be made for bringing most of the vapor into actual contact with the

[3] De Florez, *Nat. Petr. News*, 19: 32 (Dec. 7, 1927).

heated surfaces, at the same time avoiding overheating which would cause an excessive production of fixed gas. De Florez believes that the only way to accomplish this satisfactorily is to pass the gases through comparatively small tubes at very high velocity. This feature was characteristic of the Hall process which was operated for a time in England during the War, in contrast with the Rittman process which used very large tubes. The general results obtainable by this type of cracking are summarized by De Florez, who states that it is possible to obtain a yield of approximately 30% gasoline in one pass together with 12-15% of uncondensable gas. Up to the present no metal of reasonable cost has been available for the tubes, which would not be rapidly oxidized at the high temperatures required. The fuel consumption is about 10% of the total charge when no provision is made to recover heat. According to the experience of De Florez, the operating costs are approximately 25 cents per barrel of charging stock, which does not include treating or re-running of the gasoline. The "Gyro" vapor phase cracking plant operated by the Pure Oil Company at Cabin Creek, West Virginia, employs the Gray process of refining the gasoline by means of fuller's earth.

The corrosion of reaction chambers by high sulfur charging stock is apparently satisfactorily overcome by chromium plating. Chambers so plated have now been in active service for two years, using oil which normally causes corrosion at the rate of 0.5 to 0.75 inch of steel per year.

The formation of coke in the reaction chambers, hitherto one of the great bugbears of cracking at least by one well known process, has been very largely done away with by flash distillation of the hot residuum, carrying a very low level of residuum in the chambers.

The advantages of pipe stills in conjunction with bubble towers is now well recognized. Formerly, in the initial distillation of the crude, using a 36° Mid-Continent crude for the comparison, a heat input of 32% was common practice and anything better than 50% was a rare achievement. Peterkin [4] has given a comparison of former shell still practice with pipe still heating and boiler heating.

Peterkin [5] has also analyzed the consumption of steam in oil refineries, this item being the largest single item in the cost of refining petroleum and considering all finished products, is of the

4 Peterkin, *Oil and Gas J.*, 26: 64 (Jan. 5, 1928).
5 Peterkin, *Chem. Met. Eng.*, 34: 544 (1927).

COMPARISON OF HEAT BALANCE

Pipe Still *vs.* Boilers

	Shell Still Hand Fired No. 2 Buck	No. 3 Stoker Fired Boiler	Buckwheat Pipe Still	Fuel Oil Boiler	Pipe Still	Bituminous Coal Boiler Stoker Fired	Bituminous Coal Pipe Still Pulverized Coal
Total surface in radiant heat zone in per cent total surface...	50.0	20.0	5.5	20.0	16.0	20.0	16.0
B.t.u. absorbed per hour: per sq. ft radiant surface	...	13,000	11,500	13,000	9,800	13,000	9,800
per sq. ft. convection surface	. .	3,500	1,530	3,500	1,680	3,500	1,680
per sq. ft. total surface	...	5,400	2,080	5,400	2,980	5,400	2,980
Heat balance: per sq. ft. total sursorbed	32.0	72.5	56.5	81.0	76.2	75.0	75.0
Loss of moisture and hydrogen in fuel ..	4.0	4.0	4.5	7.0	7.1	5.7	4.7
Dry stack loss.....	36.0	10.9	21.0	9.0	13.2	9.8	16.7
Ash pit loss	12.0	9.1	14.0	0.0	0.0	6.5	0.1
Radiation, etc.	16.0	3.5	4.0	3.0	3.5	3.0	3.5

order of 25% of the total operating expense. The wide introduction of bubble towers for the distillation of light oils has reduced the amount of re-running with steam, and the vacuum distillation of lubricating oils is rapidly replacing the fire and steam method (see below).

Bell [6] has discussed the advantages of pipe still and bubble tower combinations and gives numerous diagrammatic flow charts and Stratford has described the adaptation of bubble towers to shell stills which were equipped with rapid forced oil circulation and forced draft heating, obtaining a throughput more than five times the former capacity of these stills. Another installation, adapting bubble towers to shell stills with other improvements at the Kanotex Refinery, raised the daily capacity from 3000 to 10,000 bbls. per day, no re-running of the gasoline and kerosene being required. Another noteworthy improvement in refinery

[6] Bell, *Nat. Petr. News,* **20**: 97 (Feb. 29, 1928).

practice has been the greater use of radiant heat in tube still heating. The data taken from the operation of a tube still, having a radiant heat section operating on Pennsylvania crude, and vaporizing 90%, have been given by Primrose.[7] This subject has also been discussed by Nash, who describes its several advantages. The heat economy, resulting from recirculating a portion of the flue gases in a convection type of furnace in connection with oil cracking, are given by Mekler.

The publication of valuable engineering data by refinery engineers is a gratifying and significant change in the policy of many companies with regard to publication. Wilson [8] has published charts for determining the sensible heat absorbed or given up by an oil for initial and final temperatures within the temperature range of ordinary refinery operations, Wilson's calculations being based upon the formula of Fortsch and Whitman.[9] A slide rule for the solution of problems of flow of gas or oil through orifices has been constructed by Schnetzler.[9a] Copies of this slide rule are distributed by the Petroleum Division of the American Chemical Society.

Sulfur continues to be the "bête noir" of many refineries. In certain of the new Texas fields the hydrogen sulfide not only causes rapid corrosion of storage tanks and lines but is a serious hazard. Mead and others have called attention to the fire and explosion hazard caused by air oxidation of finely divided iron sulfide formed by corrosion. Mead [10] has shown that if hydrochloric acid is neutralized during the distillation of crudes the corrosion is greatly reduced. In spite of the difficulties caused by corrosion, the decomposition of sulfur compounds with evolution of the sulfur as hydrogen sulfide is probably cheaper than any chemical method of removing the sulfur. Sulfur removal has been a particularly serious problem with refiners manufacturing cracked gasoline from certain California oils. Halloran [11] reports that cracked California gasolines, which apparently contain thiophenes show a loss of 30% when refined by sulfuric acid, at ordinary temperatures, to meet the specification of 0.10% sulfur. By refining with sulfuric acid at low temperatures, about $-5°$ F., the

[7] Primrose, *The Refiner*, **7**, no. 3: 87 (1928).
[8] Wilson, *Ind. Eng. Chem.*, **19**: 824 (1927).
[9] Fortsch and Whitman, *Ind. Eng. Chem.*, **18**: 795 (1926).
[9a] Schnetzler, *Ind. Eng. Chem.*, **19**: 1027 (1927).
[10] Mead, *Oil and Gas J.*, **26**: 35 (Dec. 8, 1927).
[11] Halloran, *Oil and Gas J.*, **26**: 36 (Dec. 8, 1927).

amount of acid required is reduced 40%, the solution loss reduced 30% and the polymerization loss decreased by 70%.

Faragher, Morrell and Comay [12] have investigated the thermal decomposition of some of the simple sulfur compounds, passing the vapors through hot tubes at 925° F. Considerable decomposition with evolution of hydrogen sulfide was noted at this temperature, which is about the upper temperature limit of cracking by pressure distillation, but in the case of thiophene no decomposition was observed, in the short time interval of their experiments, up to 870° C. They note that Smackover crude containing 2.5% sulfur gives less corrosion on cracking than Panhandle crude containing 0.6% sulfur, the latter yielding large proportions of hydrogen sulfide on heating. They ascribe the lesser corrosion of the Smackover oil to the stability of the sulfur derivatives present and suggest that they may be thiophenes. Youtz and Perkins [13] have compared the effectiveness of 95% sulfuric acid, anhydrous aluminum chloride and silica gel in the removal of various types of sulfur compounds from straight run gasoline. Sulfuric acid functions mainly as a solvent but aluminum chloride decomposes the disulfides, mainly to mercaptans. Hounsell [14] states that sweetening of cracked gasoline from Smackover crude is accomplished more satisfactorily by ammoniacal copper solutions than by plumbite. Morrell and Bergman [15] have prepared very useful charts showing the rate of flow of 66° sulfuric acid and 30° caustic soda through various orifices under pressure differentials up to 50 lbs. pressure, data very useful in designing continuous treating equipment.

Lubricating Oils. The distillation of lubricating oils under a high vacuum continues to be more widely practiced. Reciprocating feather valve vacuum pumps or steam jets and welded apparatus readily give the desired vacuum but the more recent developments have had to do with the method of heating. Howard and Loomis [16] have applied the principle of flash distillation. They state, "In the distillation of a typical crude oil by methods common in the petroleum industry practically three fourths of the lubricating oil fractions are destroyed. A yield of 6 to 7% of an oil having a viscosity of 285 at 100° F. is commonly obtained from Mid-Continent crude. By the vacuum distillation of the same crude

[12] Faragher, Morrell and Comay, *Ind. Eng. Chem.*, **20**: 527 (1928).
[13] Youtz and Perkins, *Ind. Eng. Chem.*, **19**: 1247 (1927).
[14] Hounsell, *The Refiner*, 7, no. 3: 59 (1928).
[15] Morrell and Bergman, *Chem. Met. Eng.*, **35**: 291 (1928).
[16] Howard and Loomis, *Nat. Petr. News*, **19**: 78 (Dec. 14, 1927).

24% of the same viscosity oil is readily obtainable." They also note that for an oil having an average molecular weight of 400, such as a Mid-Continent distillate of about 25° A.P.I., there is required 10 lbs. of steam per gallon of distillate to be equivalent to 1 inch or 25 mm. absolute pressure. Howard and Loomis also state that to a great extent the advantages peculiar to vacuum pipe still equipment are those generally claimed for pipe stills operating at atmospheric pressure. Of special importance, however, are the advantages of uniform heating by maintenance of high velocity over the heating surface, of reduced time during which the oil is subjected to heat and particularly the advantage of lower temperature due to flash distillation.

Another solution of the heat input problem in connection with high vacuum distillation of lubricating oils is the use of mercury vapor, which is being used on a large industrial scale by the Sun Oil Company. Since the boiling point of mercury at atmospheric pressure is 675° F., any temperature desired, within the range from the upper limit of steam temperatures to about 950° F., can readily be obtained by vaporizing the metal under moderate pressures or vacuum. The mercury vapor is used in very much the same way as steam, the temperature of the condensing vapor being accurately regulated by the pressure, or vacuum, maintained in the system. The apparatus is welded so that leakage and loss of mercury is nil. The metal is vaporized in a special type of boiler designed by the Babcock and Wilcox Company for the mercury vapor turbine power plant at Hartford, Connecticut. The vaporization takes place in vertical 4 inch tubes sealed at the bottom. At the Sun Oil Company plant the vapor is used under a pressure of 8 to 10 lbs. The method is particularly suited to wax-free crudes. The topped crude is treated with sufficient 50% caustic soda solution to retain the naphthenic acids and distilled in a series of fractionating sections under a pressure of 6 to 7 mm. absolute. A very small fraction of volatile malodorous oil is taken overhead and separately condensed. The resulting oils are very pale in color, stable, and are not further refined by acid or clay.

Continuous treating plants for light distillates have been in general use for about ten years, having finally almost entirely displaced batch agitators for the lighter distillates. Very little has been written regarding continuous treating systems but Morrell and Bergman [17] have recently described the design and operation

[17] Morrell and Bergman, *Chem. Met. Eng.*, **35**: 291, 350 (1928).

of such equipment. Morrell and Faragher [18] state that, when air is used in conjunction with plumbite for gasoline sweetening, the lead sulfide is oxidized to lead sulfate, which then reacts with the caustic soda to form sodium plumbite and sodium sulfate.

No particular advance has been made in the art of contact filtration of lubricating oils. The method continues to be very much discussed but very little practiced outside of California. Relative costs of contact filtration and percolation are given by Davis. [19]

Natural Gas Gasoline. The fractional distillation of "natural gasoline" to eliminate sharply the low boiling hydrocarbons is now almost universally practiced.

Butane-free natural gasoline has been advocated as an aviation fuel. It weighs 5.52 to 5.76 lbs. per gallon and has a good antiknock rating. The vapor pressures of butane-free natural gasoline range from 8 to 14 lbs. per square inch, absolute, at 100° F., the average being 11 lbs. According to Oberfell, [20] a series of commercial motor fuels showed absolute vapor pressures of 5.8 to 18.6 lbs. per square inch at 100° F., the average being 10 lbs. The addition of each percent of butane increases the vapor pressure at 100° F. by approximately 0.5 lb. per square inch.

Brown [21] has carried out a series of investigations for the Natural Gas Gasoline Manufacturers Association, and calls attention to the fact that there has been no laboratory test for measuring *volatility* of motor fuels which can be directly interpreted in terms of engine performance. Natural gas gasoline has antiknock values usually varying between 45 and 65% benzene (in a paraffin type gasoline blend). Little difference in this respect was found between natural gasolines from Eastern and Mid Continent fields. By very extensive engine tests, Brown has shown the value of natural gas gasoline in blends, in ease of starting and acceleration of the engine. In his opinion, as a result of these tests, U. S. motor gasoline is satisfactory for general service only in extremely warm weather, and gives the best performance in a warm engine only if the atmospheric temperature is above 70° F. According to Brown's tests, motor fuel for different seasons of the year should have the character shown by the following:

[18] Morrell and Faragher, *Ind. Eng. Chem.*, **19**: 1045 (1927).
[19] Davis, *The Refiner*, 7, no. 3: 90 (1928); *cf.* Lederer, *Oil and Gas J.* (Oct. 13, 1927); Historical notes bearing on contact filtration are given by Bierce, *Nat. Petr. News*, **19**: 101 (Dec. 14, 1927).
[20] Oberfell, *Nat. Petr. News*, **20**: 88 (May 23, 1928).
[21] Brown, *Trans. Am. Inst. Chem. Eng.*, Dec., 1927 (Preprint).

Temperature at Which the Indicated Percentage Should Be Distilled
in the A.S.T.M. Distillation, Corrected for Loss and Residues

Atmospheric Temperature	5-20%	30-50%	50-80%	90%
90° F.	200° F.	250° F.	350° F.	380-410° F.
60°	170°	215°	335°	380-410°
30°	140°	180°	320°	360-410°
0°	100°	150°	300°	340-410°

Lewis [22] discusses factors in the heat transmission of equipment in gasoline recovery plants and points out that condensation can take place on the cooled surface long before the gas as a whole has been cooled down to its dew point. In studying the heat transmission between a flowing mixture of steam and air, and a cooled pipe, a transmission coefficient was found which was "over tenfold what one would anticipate in view of the pipe diameter and gas velocity."

Possible uses for propane and butane separated from natural gas gasoline has been much discussed. It has been shown to be suitable for the enrichment of water gas, but its usefulness in this way has been prevented, in most localities, by economic factors, the chief of which is probably transportation cost. The gas-liquid relationships of these two hydrocarbons are as follows:

	Propane	Butane
Cu. ft. of gas at 60° F. per gal. liquid..........	38.2	32.5 .
B.t.u. per gal. of liquid.......................	96,900	106,500
B.t.u. per cu. ft. of gas at 60° F. 760 mm.......	2,519	3,274

On a B.t.u. basis it will accordingly be noted that about 10 gallons of liquid propane-butane are required to equal 1000 cubic feet of lean natural gas.

Analytical. Stevenson and Babor [23] consider that the dew point is the best indication of the temperature of complete vaporization, under equilibrium conditions of gasoline alone or mixed with air. Stevenson and Stark [24] developed their phase change method for determining the temperature of complete vaporization of gasoline at 760 mm. under equilibrium conditions. This equilibrium end point was called the Deppe end point and was proposed as a substitute for the Engler distillation. Stevenson and Babor developed their present method to apply to air-fuel mixtures.

[22] Lewis, *Trans. Am. Inst. Chem. Eng.*, 1927 (Preprint).
[23] Stevenson and Babor, *Ind. Eng. Chem.*, **19**: 1361 (1927).
[24] Stevenson and Stark, *Ind. Eng. Chem.*, **17**: 676 (1925).

There has been some controversy over the percentage of sulfur permissible in motor fuels. Diggs [25] has published the result of a coöperative study by the Standard Oil Company of Indiana and the General Motors Company. A preliminary inquiry into a number of cases of bad wrist pin corrosion developed the fact that all of these motors had been operated on benzene or benzene blends. The corrosion developed mostly in cold weather. There was no evidence that appreciable corrosion occurred in warm weather, at least with continuous running of the engine. The corrosion was due to sulfuric acid. Diggs concludes that gasoline containing "0.151% sulfur does appreciable harm, and that 0.458% sulfur does very great harm." Mougey [26] also states that although thermostats and ventilators are of very great value in combating corrosion, it is concluded that inasmuch as a large number of cars are not so equipped, an increase in the sulfur content of motor fuel is not in accord with the best interests of the automobile industry and the public. The U. S. Bureau of Mines recently reported that in an examination of 130 commercial motor fuels only seven exceeded to 0.10% sulfur limit (U. S. motor specifications).

A rapid corrosion test, described by Rue,[27] consists in shaking 100 cc. of the oil, with about 1 cc. of mercury and filtering, the amount of corrosion being judged by the mercury sulfide precipitate on the paper. This test can be carried out in about two minutes. Faragher, Morrell and Monroe [28] have published a method for determining the types of sulfur present in a motor fuel. Hydrogen sulfide is removed by cadmium chloride solution, sulfur by metallic mercury similar to the method of Ormandy and Craven,[29] mercaptans by alcoholic sodium plumbite and disulfides by reduction by zinc and acetic or hydrochloric acid. Kennedy [30] has described an improvement in the method of burning volatile fuels for sulfur determination which is used at the Bureau of Standards. A comparison of the Carius and the oxygen bomb methods for determining sulfur in heavy oils has been made by Devine and Lane,[31] who conclude that for routine work the oxygen bomb method is entirely adequate. The use of the much more tedious Carius method is necessary only when results

[25] Diggs, *Ind. Eng. Chem.*, **20**: 16 (1928).
[26] Mougey, *Ind. Eng. Chem.*, **20**: 18 (1928).
[27] Rue, *Oil and Gas J.*, **26**: 162 (May 10, 1928).
[28] Faragher, Morrell and Monroe, *Ind. Eng. Chem.*, **19**: 1281 (1927).
[29] Ormandy and Craven, *J. Inst. Petr. Tech.*, **9**, no. 26: 135 (1923).
[30] Kennedy, *Ind. Eng. Chem.*, **20**: 201 (1928).
[31] Devine and Lane, *Oil and Gas J.*, **26**: 164 (May 17, 1928).

of the highest accuracy are essential. The difference in the results by the two methods may amount to as much as 3% of the sulfur present.

Poth, Armstrong, Cogburn and Bailey [32] recommend the determination of nitrogen in petroleum oils by digesting 5 g. sample with 150 cc. sulfuric acid, 50 g. potassium sulfate, 2.5 g. mercuric oxide and 2.5 g. copper sulfate. Bailey's figures for the organic nitrogen content of California oils are very much lower than the much quoted results of Mabery. Bailey finds that, contrary to the literature, the nitrogen compounds in neither crude petroleums nor distillates can be determined by extraction with dilute mineral acids.

In a study of transformer oils, Ford [33] found that unsaturation, as indicated by loss on treating with concentrated sulfuric acid, is roughly proportional to the rate of oxidation and sludge formation. Mead [34] and collaborators measured the oxygen absorbed and finds that the temperature coefficient per increase of 10° C. is 2.4 in the range 120-130° C. Sludge formation and development of acidity start very slowly, the rate increasing as oxidation progresses. Of 177 substances added to transformer oil 48 showed a distinct inhibitory influence on sludge formation, of which three had a pronounced effect, *i.e.*, sulfur, nitrobenzol and nitrocresol.

Story and Snow [35] have shown that the cresylic acids separated by alkali from under cracked gasoline resemble those found in low temperature tars derived from coal.

The testing of the anti-knock value of gasolines has now become one of the tests carried out by every well equipped petroleum laboratory. Edgar [36] has given the results of a series of tests carried out in coöperation with other laboratories. A comparison of road tests and tests by the bouncing pin method, for determining the quantity of tetraethyl lead needed for equalizing the various motor fuels examined, was in good agreement. MacCoull [37] has also reported the results of coöperative tests of six motor fuels by ten industrial laboratories. One of the conclusions of these tests was that the measurement of anti-knock values in terms of mixtures of a reference fuel with benzene or tetraethyl lead is likely to be very misleading, if the peculiarities of such scales

[32] Poth, Armstrong, Cogburn and Bailey, *Ind. Eng. Chem.*, **20**: 83 (1928).
[33] Ford, *Ind. Eng. Chem.*, **19**: 1165 (1928).
[34] Mead, *Ind. Eng. Chem.*, **19**: 1240 (1928).
[35] Story and Snow, *Ind. Eng. Chem.*, **20**: 359 (1928).
[36] Edgar, *Oil and Gas. J.*, **26**: 34 (Feb. 2, 1928).
[37] MacCoull, *Oil and Gas J.*, **26**: 208 (May 10, 1928).

are not thoroughly understood by the investigator. Reiman [38] has given the anti-knock values of a series of commercial motor fuels, using aniline as an anti-knock reagent for equalizing the motor fuels. The following data are of interest as being comparable.

ANTI-KNOCK VALUE OF COMMERCIAL GASOLINES EXPRESSED IN PER CENT ANILINE REQUIRED BY REFERENCE FUEL TO EQUAL FUEL TESTED

Straight run, from paraffin base crude (Cabin Creek) 437°	0.50
Straight run, from Mid Continent crude, 437° end pt	0.00
Blend, 41% iso-octane, 59% n-heptane	0.00
Pressure cracked, paraffin base, 437°	0.93
Pressure cracked Mid Continent, 437°	1.45
Vapor phase cracked paraffin base, 437°	8.00
Pressure cracked California, 410°	4.50
3 cc. tetraethyl lead in 1 gal. Mid Continent	5.50
Pressure cracked Mid Continent, 400°	2.15
Pressure cracked Mid Continent, 375°	2.43
Mid Continent + 10% casinghead	0.68
Mid Continent + 25% casinghead	1.03
Mid Continent + 50% casinghead	1.98
Commercial premium anti-knock #1	3.75
Commercial premium anti-knock #2	3.75
Commercial premium anti-knock #3	3.42
Commercial ethyl gasoline #1	4.5 to 7.0
Commercial ethyl gasoline #2	4.5 to 5.5

Everyone interested in the testing of motor oils and motor fuel will find much of interest in a paper by Wilson and Barnard [39] on the significance of the tests standardized by the American Society of Testing Materials. Hill [40] has discussed the well known gasoline tests from the same practical standpoint.

Miscellaneous. The heat of solution of paraffin wax has been determined by Sullivan, McGill and French,[41] who find that wax of 125° F. melting point has a heat of solution of 40.3 Cal. per gram or 72.5 B.t.u. per lb. The same authors have determined the solubility of paraffin waxes of 111° F., 125° F. and 145° F. melting points, in petroleum ether, and in a number of Mid Continent petroleum fractions of different viscosities. Rhodes, Mason and Sutton [42] have studied the crystallizing behavior of slack wax and find, as has been shown by other recent investigations, that the relative amount of needle and plate forms of crystals is determined by the conditions under which the crystallization is

[38] Reiman, *Ind. Eng. Chem.*, 19: 1055 (1927).
[39] Wilson and Barnard, *Am. Soc. Testing Materials*, June, 1928 (Preprint).
[40] Hill, *Am. Soc. Testing Materials*, June, 1928 (Preprint).
[41] Sullivan, McGill and French, *Ind. Eng. Chem.*, 19: 1040 (1927).
[42] Rhodes, Mason and Sutton, *Ind. Eng. Chem.*, 19: 935 (1927).

carried out. The solubility of wax, melting point 56° F., in pure hydrocarbons has been determined by Weber and Dunlap.[43]

Asphalt. In spite of the increased use of concrete for road construction, it is of interest to note that the use of asphalt for this purpose continues to increase also. The production of petroleum residuum asphalt in 1927 was 3½ million tons, not including road oils, an increase of about 16% over 1926. The ratio of asphalt used for paving purposes to all other uses remains about the same, *i.e.*, about 55%. Considerable notice has been given the enormous deposits of bituminous sands, carrying about 14% of bituminous matter, occurring along the Athabasca River in Canada. But no commercial development has as yet taken place.

In Kentucky a bituminous sand suitable for road building, carrying 7% of bituminous matter, is quarried in commercial quantities.

Research. The Director of a great industrial research laboratory, well known for its theoretical researches as well as its industrial accomplishments, has stated that they had never carried out a purely scientific, theoretical investigation but what some important industrial application of it was found within two years. It is therefore very difficult, in reviewing the current technology and chemical research relating to petroleum, to determine what chemical researches may reasonably be included.

The oxidation of hydrocarbons is attracting the attention of a great many investigators. Research on the anti-knock properties of motor fuels has developed, in at least one important laboratory, into a thorough study of the chemical mechanism of the combustion of hydrocarbons. Pease and Chesebro reported at the St. Louis meeting of the American Chemical Society that in the oxidation of paraffin hydrocarbons, above ethane in the series, the reaction may start abruptly at temperatures as low as 300° C. The products of the oxidation of isobutane at relatively low temperatures are chiefly water, carbon monoxide, carbon dioxide, aldehydes, acids, olefins and simple hydrocarbons. Pease and Chesebro point out that local overheating is really molecular. It would appear therefore that the better way to control the temperature in such oxidations, to produce greater yields of the products of partial oxidation, would be dilution of the hydrocarbon-air mixture with an inert gas such as nitrogen or steam, as has been so successfully done in the catalytic oxidation of

[43] Weber and Dunlap, *Ind. Eng. Chem.*, **20**: 383 (1928).

methanol to formaldehyde. In this connection it is of interest to note that the chemists of one of the Mid Continent oil and gas companies have found that natural gas-air mixtures containing a large excess of gas can be oxidized to produce methanol and formaldehyde. These products are now being produced in this way in commercial quantities but nothing has as yet been published by the original investigators describing the process. It has been pointed out that in the manufacture of natural gasoline the material is well fractioned and the propane and usually the butane is eliminated. In refineries having large cracking plants the recovery of gasoline vapors by similar methods leads to the elimination of propylene and butene, only a very small proportion of which is now utilized for the production of alcohols. The olefins should be excellent material for study with the object of producing simple aldehydes, acetone and acetic acid.

One of the difficulties of utilizing petroleum for chemical synthesis is the number of products that must be treated. When only one or two products are desired the problem can sometimes be simplified by making use of modern methods of fractional distillation. The natural gas gasoline industry has shown that hydrocarbon fractions of two, three, four or five carbon atoms can readily be isolated. In the case of cracked gases this leads to the production of secondary alcohols of very exceptional purity. There has been much speculation as to the possibility of manufacturing synthetic rubber from petroleum. Engler and Staudinger [44] patented a method of utilizing the dienes from this source in 1912. The presence of dienes in small proportions in so-called vapor phase cracked gasoline has been suspected and Birch [45] has isolated butadiene from a low boiling fraction of the hydrocarbon "drips" separated from oil gas of the Pintsch gas type. Two gallons of the light fraction gave 292 grams of butadiene tetrabromide, corresponding to 52 grams of butadiene. It would accordingly be possible to prepare an exhibition sample of butadiene rubber made from petroleum. While it is at present obviously uneconomical to crack petroleum to produce such a synthetic product, the manufacture of a series of synthetic products, including alcohols, glycols and other obviously possible products, may conceivably be tied together to their mutual economic advantage.

[44] Engler and Staudinger, German P., 265172 (1912).
[45] Birch, *Ind. Eng. Chem.*, **20**: 474 (1928).

One of the questions repeatedly recurring in various guises, is the better utilization of methane and the simple hydrocarbons in natural gas, particularly in fields where gas is wasted or is of little or no value. The manufacture of formaldehyde and methanol, already referred to, may prove to be a partial answer. It will be recalled that the conversion of methane to hydrogen is regarded by Bergius as the saving feature of his process for the conversion of coal to oil. The methane is first converted to water gas, the carbon monoxide then reacting with another molecule of steam to carbon dioxide and another molecule of hydrogen. The most important industrial use of pure hydrogen is in ammonia synthesis. But the greatest difficulty in all of these speculations is the temporary nature of the gas supply and the comparatively unpopulated, sometimes desert character of the areas in which gas is cheap. If it were possible to move a synthetic ammonia plant around the country like a circus then this and other possibilities of utilizing natural gas would be alluring.

The recent work of Lind, reported at the St. Louis meeting, A.C.S., on the condensation of methane, ethane, propane and butane to liquid hydrocarbons by alpha radiation and by the silent electrical discharge, is of considerable theoretical interest. Oils were produced having average molecular weights varying from 105 to 467. From ethane and the higher homologues, hydrogen and methane are liberated in the proportions of about five to one, respectively. According to Lind far too much electrical energy is required for the process to be of industrial interest. Research is in progress, however, which effects similar results perhaps economically, by different methods. Hurd and Spence also reported at the St. Louis meeting on the results of cracking butane. At 600° propylene is the principal reaction product and at 700° propylene and ethylene are produced in about equal proportions.

It is a noteworthy sign of the times that the number of well-equipped research laboratories for petroleum investigation is increasing markedly.

In the petroleum industry itself several of the larger companies have built up research organizations which would be a credit to any industry. However, it is of considerable interest to note that according to a statistical analysis recently made, the average refinery represents an investment of $5,000,000, of which the amount invested in the laboratory is $10,000. Most of this investment is to provide for the necessary routine analysis and

testing. It should be remembered, however, that most of the important advances in petroleum technology in recent years have not come out of the laboratories but have been developments of engineering. The above statistical comparison may therefore not be a fair one. If all the money spent by the industry in experimental work, and including the development of cracking stills, fractionating equipment, automatic control and recording devices, improvements in the saving of heat, combating corrosion, handling emulsions, and in large scale trial of various refining and distillation methods, then the total amount would probably be a staggering one. The point is illustrated by the fact that the Bureau of Mines Experimental Station at Bartlesville, Oklahoma, has installed considerable large scale equipment for the study of problems relating to the recovery of oil from various oil bearing sands and the University of Oklahoma, which provides instruction in refinery technology under Padgett, has installed large scale experimental equipment including a 96 foot tower for the study of gas and air lift conditions and an experimental pipe still, capacity 300 bbls. per day, with a large experimental fractionating tower. There is undoubtedly a growing appreciation, however, of the importance of thorough scientific study of certain of the industries' outstanding problems. One of the most important of these is the recovery of a larger proportion of the oil occurring in the sands. Bartell and Miller, working under a grant from the American Petroleum Institute, have reported at the St. Louis meeting, on their investigation of the displacement of crude oil from sand by water and various saline solutions, a method being practiced in the Bradford, Pennsylvania, field. The University of Michigan has made a series of important contributions to petroleum technology and researches are being carried out, under grants from the American Petroleum Institute, in a number of university laboratories.

Chapter XXXVIII.

Gaseous Fuels.

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The literature on gaseous fuels during the past year has in-
cluded the usual interesting improvements in apparatus and
operating technology. Reflecting as it does the trend of interest
toward the newer developments in the industry, there is evidence
of a considerable lessening in interest toward the use of bituminous
coal in water-gas generators, gasification of the use of pure oxygen
and liquid purification, while increasing attention is being paid
to such matters as gas dehydration, naphthalene and gum removal,
the utilization of water gas in the synthesis of methane and its
higher homologs as well as methanol and other higher alcohols.

Operation and Production. A number of new processes and
improvements in apparatus are shown in the patent literature.
Yard and Percy [1] propose a process for manufacturing a gas suit-
able for domestic use by spraying oil onto a bed of incandescent
carbon and fixing these gases by passing them through a second
bed of carbon maintained at a high temperature by the conductance
of an electric current through it. A process for making mixed
water gas and coal gas has been patented by Wilcox.[2] The prin-
ciple is not new and consists of passing superheated water gas
through a bed of soft coal, thereby distilling off the coal gas.
Nielsen and Garrow [3] describe a similar process, except producer
gas is used to gasify the coal. Moorhouse [4] details a modified
method of water gas production in which a large number of
streams of air and steam are alternately passed diagonally down-
ward through the incandescent fuel. A gas producing apparatus

[1] Yard and Percy, U.S.P. 1649640 (Nov. 15, 1927).
[2] Wilcox, U.S.P. 1652386 (Dec. 13, 1927).
[3] Nielsen and Garrow, U.S.P. 1654942 (Jan. 3, 1928).
[4] Moorhouse, U.S.P. 1660202 (Feb. 21, 1928).

outlined by McDonnell [5] features the incorporation of longitudinal steam generating chambers in the walls of the producers. Clark, Loomis and Howard [6] have provided a process for the utilization of heavy asphaltic base oils for the production of gas. The mode of operation is to remove by distillation and cracking the more volatile portion while the pitchy residuum is dropped onto a bed of incandescent coke. Lummis [7] describes two forms of gas producers, the essential features consisting in a rotating shell and ash plow moving with similar or different rates of speed. A further variation in gas producer construction is introduced by the same author. It consists of an annular bottom and a device to crowd the ash inwardly to the center opening which is water-sealed by means of a flange. Cross [8] has proposed a method for making producer gas by means of powdered coal with a preheated mixture of air and steam, which are charged into a hot reaction zone where producer gas is formed.

The proposed complete automatic operation of a water-gas generator is described by Andrew.[9] This involves the use of the Steere automatic grate, which does away with the necessity of clinkering by hand. In addition, the Steere grate poker and charging machine serve to keep the fire and fuel bed in a satisfactory operating condition. A further improvement in the operation of water-gas sets as set forth by Wolfe [10] consists of an automatic volume control of steam and air applied to the set. A damper and flow measuring device are installed in the air or steam line. The damper is connected to the regulator by means of levers, while pipe connections from each side of the flow meter (Venturi, orifice, or Pitot tube) are made to each side of the regular diaphragms. Such an arrangement permits a constant rate of steam or air supply regardless of changing back-pressure conditions in the set. Willien and Stein [11] describe a modification in water-gas set operation which makes possible the manufacture of carburetted water gas having a low specific gravity. This is attained by admitting oil during the back run and most advantageously through the top of the superheater. This is the Waring process applied to back run operation. The carburetion of water gas with butane and

[5] McDonnell, U.S.P. 1662266 (Mar. 13, 1928).
[6] Clark, Loomis and Howard, U.S.P. 1651115 (Nov. 29, 1927).
[7] Lummis, U.S.P. 1655320 (Jan. 3, 1928); 1659493 (Feb. 14, 1928); 1666604 (April 17, 1928).
[8] Cross, U.S.P. 1657371 (Jan. 24, 1928).
[9] Andrew, *Gas Age-Record*, **60**: 515 (1927).
[10] Wolfe, *Am. Gas J.*, **127**, no. 8: 33 (1927).
[11] Willien and Stein, *Gas Age-Record*, **60**: 660 (1927).

propane-butane mixtures as outlined by Odell [12] consists in taking these paraffin hydrocarbons, stored as liquids under pressure, and vaporizing them into the gas stream to replace oil as the carburetting agent. The International Combustion Engineering Corporation [13] has announced a large scale installation of the K.S.G. process for the low-temperature carbonization of coal. This process was developed in Germany. The rich gas diluted with blue water gas will be sold to the Public Service Company of New Jersey.

Purification. *Sulfur Compounds.* That the problem of gas purification has not been solved satisfactorily as yet is evidenced by the frequent patents related to the removal of hydrogen sulfide and other impurities in the gas. The chemistry involved in these patents usually represents nothing new, attention being confined to improvements and modifications in operating technique. Fulweiler and Jordan [14] announce an improvement in the method of revivifying the foul solution of sodium sulfhydrate by means of finely divided air. The division of the air is effected by means of a rapidly moving paddle and the degree of dispersion regulated by the speed of the paddle. Sperr and Jacobson [15] have made provision for the disposal of the sodium thiosulfate formed in gas purification liquors. It consists of heating the material mixed with carbonaceous material and limestone so as to form sodium carbonate. Another patent by the same authors provides for the removal of hydrogen sulfide by means of a suspension of freshly precipitated iron compound in an alkaline solution and regenerating the impurity laden suspension from the gas washing operation by means of atomized air being forced through it. Bird [16] proposes a process for the removal of hydrogen sulfide by a preliminary washing with a relatively large volume of alkaline solution and a more intensive scrubbing with a smaller volume distributed over an extended surface. Jannek [17] provides for the removal of iron carbonyl vapors from gases by means of an adsorbent material. The adsorbed impurity is then destroyed by means of some chemical reagent, after which the absorbing mass is regenerated.

Outside of the patents, very little has been published during

[12] Odell, Bur. of Mines, Rept. of Investigation, no. 2840 (1927).
[13] Soule, *Gas Age-Record*, **60**: 605 (1927).
[14] Fulweiler and Jordan, U.S.P. 1632758 (June 14, 1927).
[15] Sperr and Jacobson, U.S.P. 1653933 (Dec. 27, 1927); 1656881 (Jan. 17, 1928).
[16] Bird, U.S.P. 1660741 (Feb. 28, 1928).
[17] Jannek, U.S.P. 1631823 (June 7, 1927).

the past year on the sulfur compounds present in gas. The most outstanding work was done by Huff and Holtz [18] on the origin and decomposition of carbon disulfide in gas making. Their work is a continuation of some previous research in which it was found that coal undergoing carbonization gave no carbon disulfide when the rate of change of temperature was very low, while coal undergoing a very rapid change in temperature gave important quantities of carbon disulfide. The more recent work has shown that a gas oil containing 3.31% sulfur by weight gave practically no carbon disulfide when cracked at 1200° F. However, appreciable quantities of carbon disulfide were formed as the cracking temperature was increased to 1800° F.

In an attempt to account for the origin of the carbon disulfide in the cracking of sulfur-containing gas oils a quantity of hydrogen sulfide (140 grains per 100 cubic feet) was added to the vapors of a cracked sulfur-free oil. About one-half the hydrogen sulfide disappeared without any detectable formation of carbon disulfide. However, starting with a concentration of over 3000 grains per 100 cu. ft., considerable amounts of carbon disulfide were produced with an accompanying decrease in the hydrogen sulfide. In the course of further study on the interaction between carbon and hydrogen sulfide the gas containing 200 grains of the latter per 100 cu. ft. was passed over a cartridge of sugar charcoal at a temperature of about 1550° F. At the start no hydrogen sulfide was detected in the effluent gas. After a certain time it made its appearance but the tests for carbon disulfide remained negative for a considerably longer period. At the conclusion of the experiment it was found that the charcoal had taken up from 2.8 to 5.5% of sulfur.

It is the authors' belief that the delay in the carbon disulfide formation is due to the formation of a carbon-sulfur complex, which probably plays an important part in the origin and decomposition of carbon disulfide under gas-making conditions.

Naphthalene and Gum Forming Substances. The matter of naphthalene and gum removal still remains a problem to the gas industry. Powell [19] and Powell, Merritt and Byrne [20] have described some of the latest improvements in scrubbing apparatus designed for the whole or partial removal of the above substances. Essentially the scrubber is composed of two sections; the one into

[18] Huff and Holtz, *Ind. Eng. Chem.,* **19**: 1268 (1927).
[19] Powell, *Gas Age-Record,* **61**: 141 (1928).
[20] Powell, Merritt and Byrne, *Gas Age-Record,* **60**: 3 (1927).

which the gas first enters is known as the primary or recirculating section, the other being the secondary or fresh oil section. The gas passes counter current to the flow of oil through a specially packed tower. The fresh oil which gives the gas its final scrubbing is injected periodically at a high rate of flow, thereby securing good distribution with increased scrubbing efficiency. Operating data have shown that efficient scrubbing can be accomplished with only 40 gallons of gas oil per million cu. ft.

Tar Removal. The removal of tarry particles suspended in the gas has always been a source of trouble. In recent years, this problem has been solved quite successfully by use of the Cottrell electrical precipitation process which is being installed in place of shaving scrubbers and other types of tar extractors. A very good paper describing the operation and advantages of the electrical precipitation process has been written by Sultzer.[21]

Gas Dehydration. The successful development in England of a system for the partial dehydration of gas has caused an enlivened interest among the gas engineers in this country. The method used in various gas plants in England consists of scrubbing the gas with a saturated solution of calcium chloride at the lowest feasible temperature. Bragg [22] in discussing various methods of gas dehydration mentions that of compression in particular which has been applied successfully by the Public Service Electric and Gas Company. They have found that in the high-pressure distribution mains where the gas is under a pressure of 35 to 50 lbs. there is sufficient cooling to produce a gas with a dew point of about 35° F. when expanded once more into the low pressure system. Coffman [23] recounts in detail the gas dehydration system mentioned by Bragg. He states that a comparison of meter repair costs for the year 1927 showed it was necessary to repair 35% more diaphragms in the meters taken from the division delivering the wet gas than from the division delivering partially dehydrated gas. Cleveland and Fulweiler [24] have given an outline of the various gas dehydration processes, paying particular attention to the possibilities of utilizing liquid hygroscopic substances.

Directly related to this problem of dehydration is a report on "Dust and Moisture Control" by Tomlinson.[25] This report contains the results of a series of analyses on gas main deposits found in

[21] Sultzer, *Gas Age-Record,* **61**: 505 (1928).
[22] Bragg, *Gas Age-Record,* **61**: 149 (1928).
[23] Coffman, *Gas Age-Record,* **61**: 507 (1928).
[24] Cleveland and Fulweiler, *Gas Age-Record,* **61**: 743, 749, 779 (1928).
[25] Tomlinson, *Gas Age-Record,* **60**: 811 (1927).

various localities on the Pacific Coast. Various compounds of iron were detected existing in both the ferrous and ferric states as the oxides, sulfides, sulfates and cyanides. In addition there is a description of the corrosion experiments performed by Hicks showing that neutralization of the acidic components of gas or removal of moisture would eliminate corrosion. The report is con- cluded with a discussion of the experimental results, means of preventing corrosion and a description of the chemical action of the various gaseous constituents which enter into corrosion.

Composition and Methods of Analysis. Desy [26] describes a rapid method for the colorimetric determination of carbon di- sulfide in gas which is accurate to within about 10%. The pro- cedure consists in passing the gas through an alcoholic potash solution, the carbon disulfide being absorbed to give potassium ethylxanthate. This solution is placed in a Nessler tube, acidified and treated with a solution of cupric acetate. The color of the contents of the tube is then compared with known amounts of standard potassium ethylxanthate solution treated in the same manner. Methods for determining hydrogen cyanide in gaseous mixtures have been critically studied by Seil, Skelly and Heilig- man.[27] They conclude that the sulfuric acid method is most accu- rate and preferable when a continuous sample is taken. For the analysis of a snap sample, the authors recommend the colorimetric method, since it is both rapid and accurate.

Continuing their work on the fractionation analysis of saturated and unsaturated hydrocarbons in coal gas, Yant and Frey [28] have made similar analyses of several fuel gases with special reference to illuminants. The gases analyzed were obtained by low-tempera- ture carbonization in a Karrick retort, (a) internal heating by steam at 600° C. and external heating at (b) 400° C. and (c) 850° C.; also in a McIntyre retort with external heating (d); by high temperature carbonization in a Koppers oven (e), a carburetted water gas from (f) coke and (g) anthracite, a gas obtained from the cracking of oil (h) and a mixed coal and water gas (i).

Comparison of these analyses showed that with increasing tem- perature increasing degradation of the hydrocarbons was obtained. Several samples of the extreme types of gas fractionated were also analyzed by the Bureau of Mines copper oxide Orsat method.

[26] Desy, *Gas Age-Record*, **60**: 711 (1927).
[27] Seil, Skelly and Heiligman, *Gas Age-Record*, **60**: 179, 223, 259 (1927).
[28] Yant and Frey, *Ind. Eng. Chem.*, **19**: 21, 488, 492, 1358 (1927).

The Orsat value for illuminants was found to be slightly greater, also that of methane was higher while ethane was lower. The Orsat value for nitrogen was usually 1% or so too low. The author explains this by the probability that the slow combustion copper oxide method gives too high a contraction of CO_2 and that there is also a temporary retention of combustible vapors in stopcock grease during the first part of the analytical procedure.

A piece of research which will no doubt prove to be of practical interest in the cracking of natural gas is the thermal dissociation of ethane, propane, normal butane and isobutane by Pease.[29] The experiments were carried out at 625 and 650° C. at one atmosphere pressure. The two principal reactions were dehydrogenation and demethanation and the hydrogen formed undergoes no appreciable secondary reaction. The reaction seems to be of the first order and the temperature coefficients are as a minimum 1.5-2 per 25° C. An explanation of the relative rates of the reaction is given in terms of activation energies as a function of the size of the molecule and the nature of the linkages to be broken.

Application and Utilization. Considerable research is being done at present on the effect of gases with a varying specific gravity upon the successful and efficient operation of gas appliances using these gases. Extensive investigations along this line are being conducted at the A. G. A. Testing Laboratories.[30] It is proposed to make the specific gravity tests using a coke oven gas of about 500 B.t.u. and 0.37 sp. gr. with a carburetted water gas of same heating value and about 0.65 sp. gr. For the testing of gases having various heating values, mixed, natural and water gas, both carburetted and blue, will be used.

Results of appliance tests on the admixture of natural gas with manufactured gas are described by Winterstein and Knapp.[31] It was found that 15% natural gas mixed with 85% "mixed" gas gave the most satisfactory performance without readjustment of the appliances. Using a basic mixture containing 15% natural gas and readjusted burners it was found that they would operate satisfactorily for a variation of 0 to 30% natural gas.

Much interest is being evinced over the indirect utilization of water gas as a fuel by synthesizing from it such things as

[29] Pease, *J. Am. Chem. Soc.*, **50**: 1779 (1928).
[30] Shawn, *Am. Gas Assoc. Monthly*, **9**: 411 (1927).
[31] Winterstein and Knapp, *Am. Gas Assoc. Monthly*, **10**: 27 (1928).

methane, methanol, liquid hydrocarbons (synthol), etc. Hightower and White [32] have made a study of the synthesis of methane from water gas. This study involved the conversion of mixtures of carbon monoxide, carbon dioxide and hydrogen into methane and other products at temperatures of 280-370° C., while at atmospheric pressure and in presence of a nickel catalyst. The path of the reaction as between the three equations, usually written:

$$CO + 3H_2 = CH_4 + H_2O \quad (1);$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad (2);$$
$$2CO + 2H_2 = CH_4 + CO_2 \quad (3);$$

depends upon a number of conditions. Reaction (2) appears to be uncomplicated. The question as to whether (1) or (3) dominates is largely a function of the water vapor present. Water vapor represses (1) to a marked extent. The most probable values of the equilibrium constant of the combined reactions vary from 19.4 to 22.24 at 350° C. The experimental results were in general below the theoretical.

Considerable research is also being done upon the synthesis of methanol from carbon monoxide and hydrogen. Lewis and Frolich [33] have made a study of the effect of variables on the operation of the methanol process. It was found that under given conditions the rate of methanol formation appeared to be a linear function of the rate of gas flow, although the percentage of conversion decreased due to a lessening of time of contact with the catalyst. The yield of methanol under otherwise constant conditions passes through a maximum as the temperature is raised. This is due to the formation of unfavorable equilibrium conditions and a decrease in the activity of the catalyst. The methanol produced between 300 and 350° C. at several hundred atmospheres over a catalyst of metallic oxides was found to be 99-100% pure.

Work also was done on the synthesis of alcohols higher than methanol from carbon monoxide and hydrogen under high pressure using as catalysts (1) iron impregnated with alkali and (2) mixtures of metallic oxides. In general, results obtained showed it to be very difficult to suppress side reactions leading to the formation of carbon dioxide, methane, water and elementary

[32] Hightower and White, *Ind. Eng. Chem.*, **20:** 10 (1928).
[33] Lewis and Frolich, *Ind. Eng. Chem.* **20:** 285, 354 (1928).

carbon. The liquid product usually separated in two layers—one containing water in predominating quantities, the other being of oily character and consisting of complex mixtures of the simpler oxygenated aliphatic compounds as well as hydrocarbons of varying boiling point.

Work on the synthesis of higher hydrocarbons from water gas is being carried out at the U. S. Bureau of Mines by Smith, Davis and Reynolds.[34] An extended study has been made on the action in this process of a catalyst consisting of metallic cobalt and manganese oxide with a small amount of metallic copper. Both saturated and unsaturated hydrocarbons ranging from methane up to solid paraffins have been produced. The above catalyst at the most favorable temperature (about 275° C.) takes about 1400 cubic feet of water gas to make one gallon of liquid fuel.

In a progress report of an A.G.A. sub-committee on the utilization of the off-peak water gas, Fieldner, Ernst and Brown [35] have considered the possibility of using it for the manufacture of ammonia or methanol. The ratio of the investment per annual ton of a blue gas to ammonia or methanol plant varies between 1 : 2 and 1 : 5. When the investment ratio is high such utilization of off-peak gas does not appear profitable. Other mitigating factors are the geographical distribution of the consumers of these synthetic products, particularly ammonia; the almost certain keen competition by large producers of ammonia and the reduced price due to this large scale production. Market conditions for the disposal of methanol likewise appear unfavorable until such a time when gasoline shortage provides a motor fuel market.

It would be difficult to predict the extent of application of gaseous fuels in the future. The last few years have seen the development of gas refrigeration to the point where it can compete successfully with the electric units.[36] During the course of a Natural Gas Association meeting, the local utility company [37] replaced the carburetter of an automobile truck with a gas-air mixer and operated the vehicle for twenty hours using natural gas as the fuel. The cost to run amounted to about ¾ cent per mile as compared with 2 cents per mile for gasoline. Tests have also been made, especially in Europe, on the operation of tractors by producer gas. An excellent article outlining the future trend of

[34] Smith, Davis and Reynolds, *Ind. Eng. Chem.*, **20:** 462 (1928).
[35] Fieldner, Ernst and Brown. *Proc. Am. Gas Assoc.*, Preprint (1927).
[36] Light, *Gas Age-Record*, **61:** 419 (1928).
[37] Forkner, *Am. Gas Assoc. Monthly*, **9:** 415 (1927).

developments in the manufacture and application of gaseous fuels has been written by King.[88]

The following papers were presented at the 1927 convention of the American Gas Association.

In a report on automatic clinkering and charging machines, Young summarizes the results obtained by use of the A. B. C. self-clinkering base, the Howard automatic charger and the Steere charger. Operating data and calculations furnished by Ramsburg, on the A. B. C. self-clinkering base indicate that with the adoption of an improved operating cycle 0.2 gallon less oil and 2 pounds less coke per 1000 cu. ft. are required than with the standard type machine. The percentage of steam decomposition is also higher.

Comparative operating results on a nine-foot generator using oven coke show that when equipped with the Howard automatic charger, an increased capacity of 4700 cu. ft. per hour, a reduction of 1.1 pounds of coke and 0.16 gallon of oil are obtained. Reports on the Steere charger state an opinion that it increased the capacity of the machine approximately 10%.

A report on the operation of a mechanical grate constructed by the United Gas Improvement Company is furnished by Genay. This generator has been installed on a water-gas set equipped with hydraulic operation and automatic control and so the entire operation is handled by one man. The generator is equipped with a water jacket and waste-heat boiler which furnish low- and high-pressure steam, respectively. Some of the advantages recognized are a marked increase in capacity, better utilization of waste heat for steam production and the small percentage of carbon or coke in the ash.

Considerable attention has been paid to the problem of water-gas tar emulsions. A very complete and valuable report on their prevention, treatment and utilization has been made by Seeley. An analysis of the information in regard to emulsions furnished by about 50 of the larger water-gas producers indicates that emulsion formation is due to several factors. The report contains a number of valuable suggestions for the prevention of emulsions and a brief outline of the methods used in the breaking up of the same when once formed.

Vittinghoff has outlined the recent work on gas oil efficiency and efficiency computations. Much of this work has been done under the direction of Mighill, who has sought to obtain some

[88] King, *Gas-Record*, **61**: 289 (1928).

correlation between the efficiency of the oil as determined under actual operating conditions and its chemical and physical characteristics. Relations have been established between the specific gravity of the oil and its yield per gallon in cubic feet of oil gas, as well as its B.t.u. content per pound. Such relations have made possible a very convenient modification of the "Pacific Coast Method" of calculating oil efficiencies. Mighill supplements this paper with a brief summary of various methods of analyzing gas oils for series of hydrocarbons and outlines the method whereby he obtained most consistent results.

A very complete paper on coke-fired gas producer operation was furnished by Denig. Detailed treatment was accorded the many important factors related to the production of producer gas of good quality with maximum thermal and economic efficiency. Under the different headings were considered (1) fuel, reasons for various sizes, ash content and removal and frequency of charging; (2) fire bed, proper thickness, influence of shape, freedom from blowholes, channeling and hot spots; (3) minimum carbon loss in ash and (4) steam-air ratio. Gas producer data for twenty installations are also listed. A general idea of how the various gas companies control the B.t.u. of coal gas may be gained from the sub-committee report submitted by Lohr. A report on low temperature carbonization and complete gasification by Porter gives some idea as to the quality of gas produced by the various processes both projected and operating in this country and in Europe. A very complete heat and material balance on the Glover-West continuous vertical retorts of the Stamford Gas and Electric Company has been furnished by Ward of Massachusetts Institute of Technology.

A number of papers related to the utilization of off-peak water-gas capacity have been prepared. Huff has estimated the capital investment for a blue water-gas plant to be a minimum of $75.00 and a maximum of $150.00 per M. per day. Weaver, considering the feasibility of a water-gas plant manufacturing hydrogen, points out that it offers a more promising field for the gas works than does ammonia or methanol manufacture. He suggests that a modification of the "steam-iron process" be used in which the iron oxide is reduced by the blue gas. It is estimated that the net cost of a hydrogen plant is four times that of a blue-gas plant of the same volumetric capacity.

PROBLEMS IN RESEARCH ON GASEOUS FUELS

1. The development of a laboratory method for predetermining the behavior of a coal to be used for making gas either in a coke oven or water-gas generator.

2. A cheap and efficient process for removing the so-called organic sulfur from manufactured gas. Various successful processes have been developed but are objectionable from an economic standpoint.

3. A cheap and efficient method for removal of water vapor from gas particularly in low-pressure systems.

4. Some satisfactory method of removing gum-forming substances from the gas.

5. A means of evaluating gas oils which will determine their efficiency when used for carburetting water gas.

6. Improvements in methods of analyses for impurities in the gas such as cyanogen, carbon disulfide, gum-forming constituents, organic-sulfur compounds, etc.

Chapter XXXIX.

Cellulose and Paper.

(July 1, 1926—July 1, 1928)

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A survey of the literature covering the past two years, indicates that the more important publications on cellulose have not appeared on this side of the Atlantic. In the main, American investigators (at least those whose data have been published) have contented themselves with applying the technique of European chemists, rather than in assuming leadership in the cellulose field. This surprising and deplorable situation may well be remedied in Canada in the near future, by the coöperative efforts of the Canadian Pulp and Paper Association, the Canadian Forest Products Laboratory and McGill University. Unless some similar venture is undertaken in the United States, or some large institution extends its research program, it is doubtful whether we shall have more than halting progress in our own country. The writers have had reports from time to time, that important scientific work is advancing in the laboratories of certain cellulose industries. However, there is no reason to believe that any new data gathered in this way will be published within the next few years.

Constitution of Cellulose. Hibbert and Burt[1] have continued Hibbert's studies on the reactions leading to carbohydrates and polysaccharides. In the presence of traces of sulfuric acid, methyl γ,δ-dihydroxyamyl ketone and methyl γ,δ-dihydroxybutyl ketone undergo dehydration and polymerization. Under similar conditions methyl γ,δ-dihydroxyisovaleryl ketone forms methyl heptenone oxide but shows little tendency towards polymerization.

[1] Hibbert and Burt, *J. Am. Chem. Soc.,* **50**: 1411 (1928).

The first two reactions may be analogous to the change taking place in the transformation of glucose into cellulose.[2]

The structure of ramie cellulose as derived from X-ray data has been studied by Sponsler and Dore,[3] who used stereochemical models. The cellulose is apparently made up of glucose units containing the amylene oxide ring united in chains of indefinite length by glucosidal condensation, the union between units being alternately a 1-1, and a 4-4 linkage. Data indicate that the 1-4 linkages characteristic of cellobiose are lacking. The chains of units are spaced rectangularly 6.10×5.40 Å units apart. A group of eight such units is the simplest chain which can represent the structure of ramie cellulose, which is stabilized longitudinally by primary valence forces and laterally by secondary valence forces due to the oxygen atoms. This proposed structure accounts for the tensile strength of the fibers, explains different longitudinal and lateral thermal expansions and the ordinary swelling phenomena of cellulose. Sponsler [4] has also pointed out important differences between his X-ray data and those of Herzog [5] and indicates that, if one of Herzog's values is discarded, the axial dimensions of the elementary cellulose units lose their significance.

A constitutional formula for cellulose suggested by Gray [6] consists of 24 carbon atoms with 4 anhydro-glucose residues, 3 of which contain amylene oxide rings and the 4th of which contains the butylene oxide linkage, thus giving the primary alcoholic OH group in the latter chemical properties which differ from those of the other 11 OH groups. The formula is in harmony with most present day experimental data on cellulose derivatives including cellulose xanthoanilide.[7]

Oxidation of Cellulose. The action of chromic acid on cotton cellulose has been studied by Hibbert and Hassan [8] and their results indicate the unreliability of analytical data in determining the character of oxidized cellulose. Apparently oxidation took place at the fiber surface and only small amounts of the cotton had been oxidized to form insoluble products. The greater part of the oxidizing agent was consumed in the formation of soluble products or in the complete oxidation of the cellulose to CO_2 and H_2O.

[2] *Cf.* Hibbert and Timm, *J. Am. Chem. Soc.*, **45**: 2433 (1923).
[3] Sponsler and Dore, Colloid Symposium Monograph, **4**: 174 (1926).
[4] Sponsler, *Nature*, **120**: 767 (1927).
[5] Herzog, *J. Phys. Chem.*, **30**: 457 (1926).
[6] Gray, *Ind. Eng. Chem.*, **18**: 811 (1926).
[7] Lilienfeld, British P., 231800-231811 (Apr. 4, 1924).
[8] Hibbert and Hassan, *J. Soc. Chem. Ind.*, **46**: 407T (1927).

Oxidized cellulose and uronic acids yield CO_2 and furfural, when distilled with HCl, whereas the pentosans yield only furfural and H_2O. Ritter and Fleck [9] show that catalpa wood which yields some CO_2 besides furfural under these conditions shows no increase in furfural yields as a result of chlorination by the Cross and Bevan method. The product obtained after chlorination, however, gives larger amounts of CO_2 than did the original wood. Apparently oxidized cellulose is not formed during the chlorination.

The action of sodium hydroxide on cellulose under high pressure was studied by Odén and Lindberg [10] A quantitative study of the action of eutectic mixtures of fused KOH and NaOH and cellulose was undertaken by Fry and Otto. [11] The cellulose was completely oxidized, about 95% reacting in accordance with the equation: $C_6H_{10}O_5 + 14NaOH \rightarrow 5Na_2CO_3 + (CO_2Na)_2 + 12H_2$ and the remainder according to the equation: [12] $C_6H_{10}O_5 + 8NaOH \rightarrow 4Na_2CO_3 + H_2O + 2CH_4 + 4H_2$.

Recent work on the oxidation of cellulose covering the past two years has been critically summarized by Parsons, [13] who reaches the conclusion that there are no data to justify the term "oxycellulose."

Analytical and Physical Testing Methods. Hawley and Fleck [14] have proposed a hydrolysis number for wood cellulose, which is the percentage loss obtained when one gram of Cross and Bevan cellulose is heated with 100 cc. of 15% H_2SO_4 for 3 hours. The hydrolysis number has been correlated with pulp yields.

The usefulness of the copper number, as a measure of the reducing properties of cellulose, has been seriously questioned during the past year. Gray and Staud [15] who proposed a modification of this determination, have recently shown that alkali in the modified Fehling solution partially destroys the reducing groups in cellulose, which when pretreated with alkaline tartrate solutions, shows a much lower copper number than usual. Scribner and Brode [16] have also modified Gray and Staud's procedure in tests which show a relation between copper number and folding endurance of

[9] Ritter and Fleck, *Ind. Eng. Chem.*, **20**: 371 (1928).
[10] Oden and Lindberg, *Ind. Eng. Chem.*, **19**: 132 (1927).
[11] Fry and Otto, *J. Am. Chem. Soc.*, **50**: 1138 (1928).
[12] For principles and procedure, *cf.* Fry, Schulze and Weitkamp, *J. Am. Chem. Soc.*, **46**: 2268 (1924); Fry and Schulze, *ibid.*, **48**: 958 (1926); Fry and Cameron, *ibid.*, **49**: 864 (1927).
[13] Parsons, *Ind. Eng. Chem.*, **20**: 491 (1928).
[14] Hawley and Fleck, *Ind. Eng. Chem.*, **19**: 850 (1927).
[15] Gray and Staud, *Ind. Eng. Chem.*, **19**: 854 (1927).
[16] Scribner and Brode, *Paper Trade J.*, **85**, no. 22: 47 (Dec. 1, 1927).

paper. Bentzen[17] outlines the technique for the determination of α-, β- and γ-cellulose, and Parsons [18] discusses the significance of the α-cellulose determination for the pulp industry.

The viscosity of cuprammonium solutions of cotton linters was shown by Hahn and Bradshaw [19] to be much higher than that of solutions of long staple cotton. Genung [20] has modified Small's method for determining the viscosity of cellulose solutions,[21] obtaining greater ease of manipulation with equal if not greater accuracy.

The Cellulose Division of the American Chemical Society during the past two years has had active committees dealing with the following phases of cellulose chemistry: alpha cellulose (G. J. Ritter, Chairman); copper number (E. C. Sherrard, Chairman); pentosans (W. Dore, Chairman); plasticity and viscosity (E. K. Carver, Chairman); oxidized cellulose (J. L. Parsons, Chairman); and standard cellulose (H. LeB. Gray, Chairman).

Wood, Wood Cellulose and Lignin. Harlow [22] has studied the chemical nature of the middle lamella and lignification in the secondary and tertiary layers of the cell walls of wood. According to his data, the secondary cell walls of soft wood contain appreciable amounts of lignin while those of hardwoods contain practically no lignin.[23] In either case the middle lamella is highly lignified.

The effects of partial decay and of partial hydrolysis of wood on the alkali solubility have been studied by Hawley and Campbell,[24] who have shown that total solubility in NaOH in the case of partly decayed wood is much greater than that of wood hydrolyzed to the same extent. In the former the lignin fraction is rendered much more soluble than in the latter. Hawley, Fleck and Richards [25] also studied the effects of brown and white rots (*Lenzites striata,* Swartz, and *Polystictus hirsutus,* (Shräder) Fries) on sapwood of various woods. Even in the case of white rot, cellulose is attacked before lignin. Pentosans associated with Cross and Bevan's cellulose were more readily attacked than the

[17] Bentzen, *Paper Trade J.,* **82**, no. 8: 197 (Feb. 25, 1926).
[18] Parsons, *Paper Trade J.,* **82**, no. 8: 211 (Feb. 25, 1926).
[19] Hahn and Bradshaw, *Ind. Eng. Chem.,* **18**: 1259 (1926).
[20] Genung, *Ind. Eng. Chem.,* **19**: 476 (1927).
[21] Small, *Ind. Eng. Chem.,* **17**: 515 (1925).
[22] Harlow, N. Y. State College of Forestry, Tech. Pub. no. 21 (Sept., 1927); no. 24 (July, 1928).
[23] *Cf.,* however, Ritter, *Ind. Eng. Chem.,* **17**: 1194 (1925).
[24] Hawley and Campbell, *Ind. Eng. Chem.,* **19**: 742 (1927).
[25] Hawley, Fleck and Richards, *Ind. Eng. Chem.,* **20**: 504 (1928).

cellulose hexosans. Hirt and Willets [26] have also shown that in the earlier stages of decay of white ash (by *Polyporus gilvus* (Schw.) Fries) the main source of food for the fungus is the carbohydrate material of the wood. Apparently the lignin was not appreciably attacked.

Schorger,[27] continuing his studies on gelatinization of lignocellulose, applied the viscose reaction, with simultaneous grinding, on aspen and white pine. In neither case were the carbohydrates separated completely from lignin, an appreciable part of which entered solution. The alkali soluble lignin fraction of corn cobs was shown by Phillips [28] to be a fairly homogeneous substance, with the formula $C_{40}H_{46}O_{16}$, containing four OH groups and three MeO groups. His results are in agreement with those obtained by Beckmann, Liesche, and Lehmann on winter rye straw lignin [29] and by Powell and Whittaker on flax lignin.[30]

Jahn and Wise [31] reported on the isolation, analysis and chemical properties of red spruce cellulose (*Picea rubens*). Five different methods of isolation were used. The a-cellulose from Cross and Bevan cellulose was the most homogeneous product obtained and most nearly approached cotton cellulose in its chemical properties.

Boynton and Miller [32] have extracted a *cellulase* from the anterior end of the digestive tract of the ship worm (*Bankia setacea*), which saccharifies both sawdust and filter paper.

Miscellaneous Papers and Technical Developments.   An edible rice cellulose prepared from hulls and containing 72-73% of alpha cellulose has been studied by Harding.[33] Schorger [34] has shown that Spanish moss (*Tillandsia usneoides*), which is used in upholstery, contains 46-47% cellulose, besides galactans, arabans, xylans, a phenol methyl ether glucoside (?) and non-carbohydrate materials.   .

Frolich, Spalding and Bacon [35] distilled birch wood under diminished pressure, both alone and impregnated with catalysts, using atmospheres of hydrogen, nitrogen or the gases evolved

[26] Hirt and Willets, N.Y. State College of Forestry, Tech. Pub., no. 22 (Feb., 1928).
[27] Schorger, *Ind. Eng. Chem.*, **19**: 226 (1927).
[28] Phillips, *J. Am. Chem., Soc.*, **49**: 2037 (1927).
[29] Beckmann, Liesche and Lehmann, *Z. angew. Chem.*, **34**: 285 (1921).
[30] Powell and Whittaker, *J. Chem. Soc.*, **125**: 357 (1924).
[31] Jahn and Wise, *Paper Ind.*, **10**: 244 (1928).
[32] Boynton and Miller, *J. Biol. Chem.*, **75**: 613 (1927).
[33] Harding, *Ind. Eng. Chem.*, **20**: 310 (1928); U.S.P. 1495789 and 1547582 (May 27, 1924; July 28, 1925).
[34] Schorger. *Ind. Eng. Chem.*, **19**: 409 (1927).
[35] Frolich, Spalding and Bacon, *Ind. Eng. Chem.*, **20**: 36 (1928).

during distillation. Pressure alone favors methanol formation. With the catalysts studied methanol yields usually decreased. Comparative experiments with cellulose (sulfite pulp) showed that methanol did not emanate from the cellulose.

An interesting development resulting from the work of Sheppard, Beal, Eberlin, Taylor, Chandler and Hill, all of the Eastman Kodak Company, has been the electrodeposition of cellulosic compounds.[36]

The production of alpha fiber from wood pulp by Richter of the Brown Company [37] has already been alluded to in the Annual Survey of American Chemistry, Vol. II, p. 355.

Chemical Pulp (Sulfite). Miller and Swanson,[38] in continuing their work on the chemistry of sulfite pulp, have studied the hydrolyzing action of both HCl and sulfite liquor on carbohydrates, as well as the effect of increasing temperature and acid concentration on delignification during the sulfite cook. The addition of salts of strong acids to the sulfite cooking liquor increased the rate of reaction in cooking, whereas the salts of weak acids have the opposite effect. Miller, Swanson and Söderquist [39] studied the influence of pH on sulfite cooking. They conclude that lignin removal is the result of a specific action of ionized sulfurous acid. Goodwin and Birchard [40] have investigated the effects of various catalysts in the manufacture of sulfite pulp. Swanson and Monsson,[41] by means of experimental cooks, have determined the proper temperature schedules for easy bleaching pulp, as well as the effect of pressure reduction on yields and the effect of over-bleaching on the strength of the pulp. The chemistry of the sulfite process has also been studied by Birchard [42] and by Swanson.[43]

Cameron and Phelps,[44] in a study of the hardness of sulfite pulp, conclude that residual lignin plays a part in determining pulp qualities. They give a method for approximating lignin as well as a correlation between the "lignin number" and the percentage

[36] Sheppard and Beal, U.S.P. 1589326; Eberlin and Beal, U.S.P. 1589327, 1589328; Sheppard and Eberlin, U.S.P. 1589330, 1589331, 1589332 (June 15, 1926); Taylor and Chandler, U.S.P. 1590592, 1590593; Taylor, U.S.P. 1590594; Hill, U.S.P. 1590595; Taylor, Chandler and Hill, U.S.P. 1590596; Taylor, U.S.P. 1590601, 1590603, 1590604, 1590607; Taylor and Chandler, U.S.P. 1590609 (June 29, 1926).
[37] Richter and Schur, U.S.P. 1599489 (Sept. 14, 1926); Richter, U.S.P. 1602553 (Oct. 12, 1926).
[38] Miller and Swanson, Tech. Assoc. Papers, 9: 118 (1926).
[39] Miller, Swanson and Söderquist, Tech. Assoc. Papers, 9: 123 (1926).
[40] Goodwin and Birchard, *Paper Ind.*, 8, no. 4: 617 (1926).
[41] Swanson and Monsson, Tech. Assoc. Papers, 9: 127 (1926).
[42] Birchard, *Paper Trade J.*, 85, no. 12: 59 (1927).
[43] Swanson, *Paper Trade J.*, 83, no. 22: 46 (1926).
[44] Cameron and Phelps, *Paper Trade J.*, 83, no. 21: 39 (1926).

lignin. Birchard [45] has studied the factors influencing the blackening of pulp during the sulfite digestion. This same investigator [46] has compared the methods used in titrating sulfite cooking acid and concludes that the iodate method is the best and most convenient.

Cable [47] has made a careful study of cooking conditions for spruce by the sulfite process, and has confirmed Miller and Swanson's finding that reducing sugars in the spent sulfite liquor are comparable in amount with those produced by hydrolysis with sulfuric acid. He has studied the effect of cooking in the presence of calcium, magnesium, mixtures of calcium and magnesium, and of sodium and ammonium bisulfites and finds that the yield is the same regardless of the base used. He also gives data on the results of cooking with and without an excess of SO_2. Hausen [48] has given a comprehensive review of patents and articles dealing with processes in which alkalies are substituted wholly or in part for the usual alkaline earths. Monsson [49] has pulped various hardwoods by the sulfite process obtaining pulps suitable for paper or board, provided a high free SO_2 content and a long period of impregnation were used. A semi-chemical pulping process, producing pulp suitable for boards or low grade printings, has been described by Rue, Wells, Rawling, and Staidl. [50] Pressure impregnation with cooking liquors, followed by mild digestion of chips with nearly neutral chemicals (Na_2SO_3 and $NaHCO_3$), was used. These in turn were followed by mechanical treatment of the chips in a rod mill.

The chemistry of pulping flax straw by means of aqueous Na_2SO_3 at 155° C. was studied by Bray and Peterson. [51] Changes in sulfite concentration, between 40 and 80 grams per liter, had little effect on the properties of the product. However, increase in the ratio of weight of chemical to straw caused an acceleration in the rate of delignification.

Campbell has made a study of SO_2 solutions. [52]

Chemical Pulp (Soda Process). Cable, McKee, and Simmons [53] have studied the effect of chip length on the yield and quality of the soda pulp obtained from a number of species. These

[45] Birchard, *Paper Trade J.*, **85**, no. 23: 49 (1927).
[46] Birchard, *Paper Ind.*, **8**, no. 5: 793 (1926).
[47] Cable, *Paper Trade J.*, **85**, no. 13: 43; no. 14; 58 and no. 15: 50 (1927).
[48] Hausen, *Paper Trade J.*, **84**, no. 9: 51 (1927).
[49] Monsson, *Paper Trade J.*, **86**, no. 17: 59 (1928).
[50] Rue, Wells, Rawling and Staidl, *Paper Trade J.*, **83**, no. 13: 50 (1926).
[51] Bray and Peterson, *Ind. Eng. Chem.*, **19**: 371 (1927).
[52] Campbell, *Pulp Paper Mag. Can.*, Inter. No., **1927**: 140.
[53] Cable, McKee and Simmons, *Paper Trade J.*, **83**, no. 14; 47 (1926).

same investigators [54] made an experimental study of the yields and quality of soda pulp obtained from birch and maple, with reference to the effect of variations in cooking time and causticity on yields and bleach consumption. Apparently the yields and character of hard maple pulp favor its use.

An anonymous author [55] describes an experimental plant using the Dorner process for the conversion of cornstalks into pulp. It entails essentially a soda cook, after the removal of water soluble materials.

Shafer, Bray and Peterson [56] have studied the amount of chlorine needed to complete pulping of flax straw after treatment with NaOH. They find that, as the amount of NaOH used increases, chlorine consumption decreases. Bray and Peterson [57] and Schafer and Peterson have made a further study on hydrolysis and delignification of flax straw with alkaline reagents (NaOH and $NaOH + Na_2S$).

De-Inking of Paper. Briggs and Rhodes [58] made a quantitative study of the de-inking process showing the effect of detergents and giving specifications for an ideal de-inking reagent. O'Connor [59] has also studied the de-inking and washing of waste paper stock and gives experimental data on the use of NaOH as compared to Na_2CO_3 with respect to quantities used, color and product. NaOH is better on hard sized papers, while Na_2CO_3 is better for soft sized paper. While not a chemical process it is interesting to note the new method devised by Mason [60] for producing pulp from steam-exploded wood. The use of this product has been confined to date to the production of pressboard and insulating board.

Bleaching. Curran and Baird [61] have studied the effect of consistence on the bleach ratio and conclude that increase of consistence does not effect the final color, provided the bleach ratio is just low enough to produce low or average bleach. If a high ratio is used to produce a very white pulp, there is a gain in using high consistence. Bleaching at high consistencies gives products

54 Cable, McKee and Simmons, *Paper Trade J.*, **82**, no. 8: 158 (1926).
55 *Ind. Eng. Chem., News Edition*, **6**, no. 10: 1 (1928).
56 Shafer, Bray and Peterson, *Paper Trade J.*, **84**, no. 8: 207 (1927).
57 Bray and Peterson, *Paper Trade J.*, **86**, no. 3: 48 (1928); Schafer and Peterson, *ibid.*, **86**, no. 3: 51 (1928).
58 Briggs and Rhodes, *Colloid Symposium Monograph*, **4**: 311 (1926).
59 O'Connor, *Paper Mill*, **49**, no. 40: 10 (1926).
60 Mason, *Paper Trade J.*, **83**, no. 3: 47 (1926).
61 Curran and Baird, *Paper Trade J.*, **84**, no. 15: 45 (1927).

slightly lower in a-cellulose. High consistencies require longer bleaching periods.

Lime for absorption of chlorine in paper-mill bleach liquor practice has been studied by Hooker.[62]

Paper Making and Beating. Spence [63] has presented a paper giving the sources of foam on paper machines and explained in part the chemical causes and means of avoiding them.

Taylor [64] has discussed hydrogen-ion concentration and its application to pulp and papermaking. An extensive and careful investigation of the uses of hydrogen-ion methods in the control of pulp and paper manufacture, has been made by Franke and Willaman.[65] While the hydrogen electrode gives valuable information regarding many pulp mill liquors, it is unreliable in testing sulfite solutions with pH $<$ 7.0. The quinhydrone electrode proved generally untrustworthy. The antimony electrode was the most generally useful, since it required no hydrogen, was inert towards sulfites, gave a fairly quick response and was well adapted for continuous reading and recording instruments. Morgan and Libby [66] have shown that hydrogen-ion concentration has a definite effect on the hydration of cellulose. Cotton cellulose shows minimum hydration at pH 4-4.5 and also at about pH 10.5. Maximum hydration was reached at pH 8.5. The effect of hydrogen-ion concentration (above pH 7) on sulfite pulp was not the same as for cotton cellulose; in fact in case of the former, a minimum hydration was developed at pH 8-9, while a maximum point was noted at pH 10.7. Strength tests gave a more accurate measure of hydration than did slowness tests.

Hoffman [67] has studied the effect of residual acid on the rate of deterioration of paper. The results are extremely useful from the standpoint of control. An anonymous writer [68] gives a résumé of an experimental study on the effect of additional amounts of glue in surface sizing on physical tests. This also includes the effect of adding hardening materials, lubricants, etc. (on physical tests). Hammill, Gottschalk, and Bicking [69] have made laboratory and experimental (semi-commercial) studies, comparing glue with

[62] Hooker, *Ind. Eng. Chem.*, **19**: 712 (1927).
[63] Spence, *Paper Trade J.*, **86**, no. 9: 53 (1928).
[64] Taylor, *Paper Trade J.*, **82**, no. 8: 166 (1926); *Paper Ind.*, **9**, no. 7: 1144 (1927).
[65] Franke and Willaman, *Ind. Eng. Chem.*, **20**: 87 (1928).
[66] Morgan and Libby, *Paper Trade J.*, **85**. no. 19: 55; no. 20: 52 (1927).
[67] Hoffman, *Paper Trade J.*, **86**, no. 9: 58 (1928).
[68] *Paper Trade J.*, **83**, no. 7: 54 (1926).
[69] Hammill, Gottschalk and Bicking, U.S. Bur. Standards, *Tech. Paper* 323 (1926); *Paper Trade J.*, **83**, no. 19: 42 (1926).

casein for coating purposes. Steadman [70] discusses means of in creasing the suspension of the coating mixture by the addition of colloids. Pitch in pulp and paper mills is discussed by Campbell.[71] He indicates the pH at which pitch on the machine is at a minimum and also discusses the causes of pitch trouble.

Paper Testing. Very recently, a committee of the Technical Association of the Pulp and Paper Industry has compiled, in book form, the paper testing methods used in the U. S. A.[72] A valuable bibliography is included. As usual, official paper testing methods of the T. A. P. P. I. have also been published from time to time in the appropriate trade journals.[73]

Pulp Testing. Davis has made a number of studies on the "freeness" of sulfite pulp [74] and of groundwood pulp.[75] Equipment used in freeness testing has also been described and discussed.[76] Strength testing of pulp (as a measure of hydration) has also received considerable attention.[77]

Raw Materials and Their Control. Dreshfield [78] has criti cally discussed methods for rosin size analyses and gives what he considers the most valuable control methods for size. Dorr and Bull [79] have made a careful study of limes used for caustic izing purposes. The effects of excess lime on the rate of settling and of temperatures and agitation during causticizing, are dis cussed. Textor and Hoffman [80] have studied soda estimation by electrical conductivity methods. The possible uses of manila rope waste and waste mail pouches as raw materials in papermaking have been studied by Shaw and Bicking.[81] The same authors [82] also studied papermaking qualities of Brazilian Caroa fiber, and of *Stipa ichu* Grass (from Ecuador).[83] The latter was shown to be an unpromising raw material.

[70] Steadman, *Paper Trade J.*, **82**, no. 8: 209 (1926).
[71] Campbell, *Paper Ind.*, **8**, no. 11: 1912 (1927).
[72] "Paper Testing Methods." New York, Lockwood Trade. J. Co., **1928**. 126 p.
[73] *Paper Trade J.*, **83**, no. 11: 55 (1926); **84**, no. 4: 48; **85**, no. 19: 60; no. 23: 62 (1927); **86**, no. 8: 209 (1928).
[74] Davis, *Ind. Eng. Chem.*, **18**: 631 (1926); **19**: 162 (1927).
[75] Davis, *Ind. Eng. Chem.*, **19**: 84, 1927).
[76] *Paper Trade J.*, **85**, no. 4: 52 (1927); *Paper Ind.*, **8**, no. 6: 999 (1926).
[77] *Paper Trade J.*, **84**, no. 4: 47; no. 8: 169 (1927); **85**, no. 11: 51 (1927); **86**, no. 8: 199 (1928).
[78] Dreshfield, *Paper Trade J.*, **86**, no. 21: 59 (1928).
[79] Dorr and Bull, *Paper Trade J.*, **84**, no. 21: 41 (1927).
[80] Textor and Hoffman, *Paper Trade J.*, **83**, no. 8: 201 (1927).
[81] Shaw and Bicking, *Paper Trade J.*, **84**, no. 18: 68; no. 19: 45 (1927).
[82] Shaw and Bicking, U.S. Bur. Standards, *Tech. Paper* no. 340 (1927). 24 p.
[83] Shaw and Bicking, *Paper Trade J.*, **83**, no. 18: 105 (1926).

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Chapter XL.

Rayon.

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Industrial Progress. The past year has witnessed the continued growth and expansion of the rayon industry. Production in the United States for the year 1927 showed an increase of 20% over 1926. No significant price changes were experienced during the year; the average price of "A" grade 150 denier yarn remaining at $1.50 per pound. Prices in general have reached a rather stabilized figure and are not expected to drop radically except as production costs are gradually pared down.

Two of the large producers of rayon by the viscose process have lately announced their plans to also enter the field of cellulose acetate yarns. Several additions to existing viscose plants have recently been made or are under way at this time.

The following tables summarize the commercial progress of the past year.

TABLE I

RAYON PRODUCTION BY COUNTRIES—1927 [1]

Country	1926 Production Pounds	1927 Production Pounds
United States	62,575,000	73,300,000
Great Britain	25,500,000	38.803,000
Italy	35,000,000	36,000,000
Germany	26,000,000	31,000,000
France	17,500,000	21,000,000
Belgium	13,100,000	13,500,000
Switzerland	8,000,000	10,340,000
Japan	5,500,000	8,000,000
Poland	....	4,000,000
Austria	....	3,500,000
Czechoslovakia	....	3,500,000
Spain	....	1,000,000

[1] *Textile World*, 73: 2903 (1928).

TABLE II

Domestic Rayon Production by Manufacturers [2]

Company	Process	1926—Lbs.	1927—Lbs.	1928—Lbs. Predicted
Viscose Company	Viscose	37,000,000	41,000,000	51,000,000
DuPont Rayon Company	Viscose	10,900,000	15,100,000	19,000,000
Tubize Artificial Silk Co.	Nitrocellulose	7,000,000	7,500,000	9,500,000
Celanese Corp. of America	Acetate	2,500,000	3,500,000	5,000,000
Industrial Rayon Corp..	Viscose	3,400,000	3,450,000	4,250,000
Belamose Corporation ...	Viscose	875,000	1,400,000	1,700,000
Delaware Rayon Company	Viscose	......	500,000	1,400,000
Acme Rayon Corporation	Viscose	400,000	500,000	650,000
Other firms	Viscose	500,000	2,100,000	3,000,000
Total............................		62,575,000	75,050,000	95,500,000

Several manufacturers have been putting out a partially de-lustered rayon in small quantities to meet the demands, particularly of the hosiery trade, where the high luster of ordinary rayon is often considered objectionable. A number of after-treatments of skein rayon, which may be applied by the finisher, effect a partial delustering but where such treatments involve the pre-cipitation on the fiber of heavy metal salts, such as barium sulfate, tin phosphate, etc., there is likelihood of seriously weakening the threads. The demand for delustered yarns, therefore, is more likely to be successfully met by the rayon manufacturers themselves through modification of certain steps in their processes which will not adversely effect the quality or strength of the delustered thread.

New Cellulose Spinning Solutions. The scarcity of pub-lished American contributions to the knowledge of the chemical aspects of rayon continues. The chief advances and contributions to this art are still coming from abroad. The majority of American patents issued within the past year cover relatively minor improve-ments or advances in the general chemical aspects of rayon manu-facture and spinning.

An interesting new cellulose product suitable for spinning has been disclosed by Lilienfeld,[3] who acts on cellulose xanthic acid (viscose) with a monohalogen derivative of a fatty acid, form-ing cellulose-thion-thiol-carbon-hydroxy paraffin monocarboxylic acids. These bodies may be precipitated from aqueous solutions by drying at atmospheric or reduced pressures and form water-insoluble products. They can be so manipulated as to form con-tinuous threads, filaments or bands.

[2] *Textile World*, 73: 686 (1928).
[3] Lilienfeld, U.S.P. 1642588 (Sept. 13, 1927).

Cellulose formates have long been patented in spinnable solutions but the process yielded a brittle product. Jurling [4] now claims to have overcome some of the inherent defects of former products by treating cellulose with high concentrations of formic acid at temperatures of 0-5° C. or below, in the presence of a catalyst and a condensing agent. The formate solution may be spun into an aqueous bath containing a salt of formic acid to form continuous threads of superior strength and luster.

New mixed cellulose esters of cellulose are described by Berthon,[5] who prepared the nitro- and acetylcellulose laurates. These products possess film and thread forming properties.

Viscose Process. The dyeing of viscose fibers in the process of manufacture is improved by Mendel,[6] who treats the threads before or during dyeing with a 3% trisodium phosphate solution at 50-100° C. Phosphates are also used by Neidich [7] in a coagulating bath of somewhat higher acid content than customary and in conjunction with a high viscosity viscose. The effect is one of forming an outside, initially coagulated sheath on the filament before the interior sections are coagulated. Threads from this process possess a scintillating luster. Phosphates are also claimed to inhibit the deposition of sulfur in the thread during coagulation.[8]

Highly extensible threads from viscose are claimed by Neidich,[9] who carries out the initial dehydration of spun threads in an atmosphere of alcohol vapors.

Slight modifications in the well known use of zinc sulfate in coagulating baths for viscose are proposed by Niederhauser and Kline.[10] Unripe viscose is spun by Kämpf [11] into an acid bath containing products resulting from the treatment of wood with phenol and sulfuric acid. An acid bath containing sugar is patented by Huttinger.[12]

A spinnerette alloy of gold and nickel is proposed by Williams.[13] A means for producing the fine holes in spinnerettes is described by Jones.[14]

[4] Jurling, U.S.P. 1656119 (Jan. 10, 1928).
[5] Berthon, U.S.P. 1651990, 1651991 (Dec. 6, 1927).
[6] Mendel, U.S.P. 1633220, 1633221 (June 21, 1927).
[7] Neidich, U.S.P. 1643080 (Sept. 20, 1927).
[8] Mendel, U.S.P. 1646625 (Oct. 25, 1927).
[9] Neidich, U.S.P. 1651404 (Dec. 6, 1927).
[10] Neiderhauser and Kline, U.S.P. 1661493, 1661574 (March 6, 1928).
[11] Kämpf, U.S.P. 1654818 (Jan. 3, 1928).
[12] Huttinger, U.S.P. 1646538 (Oct. 25, 1927).
[13] Williams, U.S.P. 1647822 (Nov. 1, 1927).
[14] Jones, U.S.P. 1654936 (Jan. 3, 1928).

Purification of rayon "cakes" or skeins for copper removal is effected by Gladding and Sharpe [15] by treating with an alkali metal cyanide. Washing and purification of rayon "cakes" from the centrifugal pot process is carried out by McKenzie [16] by supporting the cake on a spindle rotating at high speed and allowing the purifying solutions to penetrate from the inside by the action of centrifugal force. Intermittent washing of masses of fibers is proposed by Neidich.[17]

The prevention of volatile sulfur compounds from escaping into spinning rooms is effected by Niederhauser and Kline [18] by treating cellulose xanthate with carbon dioxide, which in part decomposes the undesirable products that might tend to contaminate the factory air. Kempter,[19] on the other hand, makes no attempt to remove excess carbon bisulfide after xanthation, claiming that a better viscose solution is obtained and that filtration is improved.

Cellulose Acetate Process. Considerable activity still exists in discovering means of cheapening and improving the cellulose acetate process. Chromium compounds are proposed by Levy [20] as catalysts in the acetylation reaction. A suppressed degradation of the cellulose is said to result through their use. Zdanowich [21] spins an acetate solution into a bath with little or no tension on the thread. Clément and Rivière [22] use a saponifiable oil as a setting bath. Malm [23] proposes perchlorates, preferably those of heavy metals, for catalysts in the acetylation reaction. Lahousse [24] produces hollow filaments from cellulose acetate by carefully controlling the temperature of evaporation of the solvent above its boiling point during spinning of the ester. Mallabar [25] acetylates in the presence of only small quantities of zinc chloride after previous treatment of the cellulose with acetic and sulfuric acids. The product so prepared is said to resist charring by heat.

Miscellaneous. *Films.* Viscose is coagulated in the form of a film on a moving carrier by the process of Czapek and Weingand,[26] wherein it passes through alkaline, neutral and acid zones

[15] Gladding and Sharpe, U.S.P. 1655097 (Jan. 3, 1928).
[16] McKenzie, U.S.P. 1648619 (Nov. 8, 1927).
[17] Neidich, U.S.P. 1654552 (Jan. 3, 1928).
[18] Niederhauser and Kline U.S.P. 1655709 (Jan. 10, 1928).
[19] Kempter, U.S.P. 1656120 (Jan. 10, 1928).
[20] Levy, U.S.P. 1652024 (Dec. 6, 1927); U.S.P. 1655870 (Jan. 10, 1928).
[21] Zdanowich, U.S.P. 1630285 (May 31, 1927).
[22] Clément and Rivière, U.S.P. 1634980 (July 5, 1927).
[23] Malm U.S.P. 1645915 (Oct. 18, 1927).
[24] Lahousse, U.S.P. 1652206 (Dec. 13, 1927).
[25] Mallabar, U.S.P. 1652573 (Dec. 13, 1927)
[26] Czapek and Weingand, U.S.P. 1641322 (Sept. 6, 1927).

in a bath through which an electric current is passing. Curved sausage casings are cast from viscose in a process described by Henderson.[27] Leaver [28] casts seamless hollow or molded articles from viscose.

Sources of Cellulose. Several new sources of cellulose for rayon manufacture have been recently proposed. These include corn stalk pulp [29] and sequoia bark.[28] Jackson [30] discusses several dozen possible sources of cellulose and their relative merits.

At the present time purified cotton linters and high alpha wood cellulose constitute the only raw materials for rayon manufacture on a commercial scale. Although new pulps suitable for this industry may logically be expected to develop, there has been a decided failure of many investigators in the past to appreciate the rigid requirements which the rayon process imposes on its raw material. For this reason there have appeared, from time to time, rather extravagant claims for the suitability of one or another type of cellulose for the rayon process.

Dyeing and Finishing. The increased use of rayon has gone hand in hand with improved methods of knitting, weaving, dyeing, and otherwise converting the fiber to a salable article. A considerable literature is accumulating relative to the mill handling, dyeing and finishing of rayon yarns or fabrics.

Morningstar,[31] Greenhalgh,[32] Mullin,[33] Herstein,[34] Harris [35] and others have contributed to the practice of bleaching, dyeing and handling of the different types of yarn.

Sturtevant [36] discusses recent development in rayon uses.

The textile trade journals are carrying quite a volume of miscellaneous empirical information, hints and suggestions for the rayon finisher. A review of this material does not come within the scope of this chapter, although much of it has assisted converters of yarn to a better understanding of the properties and behavior of the new fiber with which they are working.

[27] Henderson, U.S.P. 1645050 (Oct. 11, 1927).
[28] Leaver, U.S.P. 1659033 (Feb. 14, 1928).
[29] *Chemicals*, 29, no. 7: 32 (1928).
[30] Jackson, *Textile World*, 73: 1291 (1928).
[31] Morningstar, *Proc. Am. Assoc. Textile Chem. Colorists*, 1927: 241.
[32] Greenhalgh, *Dyer, Calico Printer*, 58: 160 (1927).
[33] Mullin, *Textile Colorist*, 49: 101, 173, 178 (1927).
[34] Herstein, *Rayon J.*, 2, no. 10: 13 (1927).
[35] Harris, *Textile Colorist*, 49: 615 (1927).
[36] Sturtevant, *Textile World*, 71: 319, 1198, 1741, 2643, 3259, 3971; 72: 329, 862, 1731, 2543, 2884, 3677 (1927); 73: 208 (1928).

Chapter XLI.

Explosives.

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Hercules Powder Company

Coal dust and other dusts have received a good deal of atten- tion during the past year. The Bureau of Mines [1] investigated the explosibility of Utah coal dust, finding that 62-67% of rock dust was required to prevent explosion when no gas was present, 70-74% when 1% of gas was present, and for each additional per cent of gas 12-14% additional rock dust to prevent explosions from blown-out shots of 4 lbs. of black powder. Rice, Paul and Greenwald [2] describe tests in the experimental mine of the Bureau of Mines from 1919 to 1924 inclusive, finding no strik- ingly new facts but in general confirming those found previously. Kepner [3] found that ignition of sulfur dust was probably due to impact of sulfur on the iron bracing rods of bins. Brown [4] re- views measures for preventing dust explosions and tests in a building having hinged windows to vent automatically the pres- sure of explosion. Stinson [5] patents a spray composed of a solution of sulfuric acid, sodium bicarbonate, etc., to render dust non- explosive. Trent [6] treats mine surfaces with a high-boiling oil to retain coal dust.

Gas explosions have received their share of attention. Brown and Watkins [7] prepared mixtures of pure liquid fuels and oxygen, added varying amounts of nitrogen and exploded the mixtures in a bomb. The amounts of nitrogen necessary to add to reduce the violence of the explosion to an arbitrary standard varied directly as the rate of rise of pressure, as does the velocity of flame travel.

[1] Greenwald, Bur. of Mines, *Tech. Paper* 386 (1927).
[2] Rice, Paul and Greenwald, Bur. of Mines, *Bull.* 268: 1-168 (1927).
[3] Kepner, *Ind. Eng. Chem., News Ed.*, 5: 2 (Jan. 10, 1927).
[4] Brown, *Quarterly Nat. Fire Protection Assoc.*, 21: 47 (1927).
[5] Stinson, U.S.P., 1612072 (Dec. 28, 1926).
[6] Trent, U.S.P., 1642912 (Sept. 20, 1927); U.S. reissue, 16914 (Mar. 20, 1928).
[7] Brown and Watkins, *Ind. Eng. Chem.*, 19: 363 (1927).

Ingham [8] found that explosions in crank cases are due to over-heated cross-head guides and that methods of prevention were obvious. Perrott and Gawthrop [9] devised apparatus for photographing on a moving film the phenomena occurring when a charge of explosive is fired into a combustible mixture of gas and air. Richardson and Sutton [10] describe apparatus in which the range of vapor concentrations in air has been determined for a number of typical lacquer solvents, both single and mixed, concluding that solvents of the alcohol and ester types require a greater concentration than the hydrocarbon diluents. The medium and high-boiling alcohols and esters are incapable of forming explosive mixtures with air, even though the alcohol and ester are of the high-boiling types. Ventilation was adequate in the booths tested.

Leybold [11] describes how a broken cylinder head of an ammonia compressor allowed quantities of ammonia gas to escape into an engine room, causing an explosion. Experiments showed that mixtures of air and 17 to 27% ammonia at ordinary pressures can be exploded by a flame, generating a pressure of 6 atmospheres or about the same as with hydrogen-air mixtures. Open lights should be avoided in rooms containing refrigerating apparatus. Gill [12] describes two curious explosions resulting from backing up of gasoline from long-abandoned gasoline-gas generators into cellars by flooding.

A curious explosion is described by van Brunt.[13] A carboy containing ammonia liquor was used as an egg to elevate ammonia liquor. To avoid excess pressure an iron U-tube containing mercury was attached as a safety valve. This device had been in use daily for ten years, when a violent explosion occurred, limited to a small area on the ammonia side of the U-tube, opening the iron pipe for about four inches. The explosion may have been due to a mercuri-ammonium oxide, formed at room temperatures by the long exposure of mercury oxide to ammonia gas.

Jones and Perrott [14] found that under normal conditions in a mine, with methane as the only flammable gas present, the atmosphere ceases to be flammable if the oxygen content is reduced to 12%. Under abnormal conditions, such as following a mine fire,

[8] Ingham, *Power*, **66**: 400 (1927).
[9] Perrott and Gawthrop, *Ind. Eng. Chem.*, **19**: 1293 (1927).
[10] Richardson and Sutton, *Ind. Eng. Chem.*, **20**: 187 (1928).
[11] Leybold, *Gas- und Wasserfach*, **70**: 40 (1927); Am. Gas. Assoc., Bull. Abstracts July 1, 1927.
[12] Gill, *Quart. Nat. Fire Protection Assoc.*, **20**: 369 (1927).
[13] Van Brunt, *Science*, **65**: 63 (1927).
[14] Jones and Perrott, *Ind. Eng. Chem.*, **19**: 985 (1927).

when several combustible gases are present, the oxygen content must be reduced below 12%, the extent depending upon the character of the atmosphere. In all sealed-off places the oxygen should be reduced to 5%. At temperatures above those at which rescue workers could stand, a still greater oxygen reduction may be required.

Price [15] describes an explosion at Detroit due to pyroxylin lacquer dust, costing 28 lives and causing about $4,500,000 damage. He also reviews dust explosions in many other industries, showing this menace to industry to be very widespread.

Van Gelder and Schlatter [16] have compiled a very comprehensive history of the explosives industry in America.

Methods of testing explosives have not been neglected. Ford [17] describes at length instruments for determining ballistics, muzzle velocity and pressures at the Aberdeen Proving Ground. Dehn and Wagner [18] applied the sand test to military explosives, finding that sensitive mixtures respond to the test readily, while the insensitive ones must be well confined. The maximum explosive strength was when yielding carbon monoxide or dioxide. These tests compared well with other methods of determining strength. LaMotte [19] describes sensitiveness tests, the so-called gap test, in which a cartridge is cut in half, a cap inserted into the closed end of one half, the two halves placed at measured distances apart with their cut ends facing, rolled in a sheet of Manilla paper, placed on the ground and detonated. The maximum distance at which the second half will detonate is the criterion. This test is only useful to determine change in sensitiveness of a certain explosive with age and not to distinguish between explosives, the differences shown by different explosives being very much greater than those produced by deterioration of the explosive. The gap test of a 60% straight dynamite may be over 48 inches, of a 20% gelatin dynamite 4 inches, while a nitrostarch dynamite, which propagates detonation indefinitely when confined, usually gives a gap test of 1 to 2 inches. Certain explosives which detonate by 1 to 2 grains of fulminate give no gap, while others, requiring 4 to 5 times as much fulminate to detonate, give a gap of several inches. The test should be made with 1.5 inch cartridges, the two

[15] Price, *Chem. Met. Eng.*, **35**: 150 (1928).
[16] Van Gelder and Schlatter, *History of the Explosives Industry in America*. New York, Columbia Univ. Press, 1927. 1132 p.
[17] Ford, *Army Ordnance*, **7**: 113 (1926).
[18] Dehn and Wagner, *Army Ordnance*, **8**: 35 (1927).
[19] La Motte, duPont Explosives Service Bull., March, 1927. 3 p.

halves of which are wrapped in three turns of case lining paper and detonated at 70° F., because sensitiveness of any dynamite falls appreciably at lower temperatures but does not rise materially at reasonable increases above this point. Taylor and Rinkenbach [20] determined the sensitiveness of detonating compounds to frictional impact, impact and heat, using a pendulum friction machine like the standard machine at the Bureau of Mines but built to one-quarter the scale. The sensitiveness to impact was determined on a modified impact machine, and sensitiveness to heat by a metal bath.

Jones [21] gives location, construction and protection of magazines for explosives, with plans, details and rules governing distances from each other and from other buildings, depending upon the quantity of explosives involved. Detonators must be stored separately.

Wöhler [22] patents a method of testing detonators by detonating by a blasting cap various mixtures of trinitrotoluene and paraffin oil, the quantity of paraffin oil present being the criterion.

Jones and Perrott [23] tested gelatin dynamites of varying oxygen balances in the Bichel gauge, the Crawshaw-Jones "dumb-bell" and the Hercules Powder Company buried tank. They found a straight line existing between oxygen balance and carbon monoxide produced, with a given apparatus and with explosives having a negative oxygen balance. Increased confinement decreased the amount of carbon monoxide produced by such explosives. Gelatin dynamite, detonated under confinement as in actual practice, always produced small amounts of carbon monoxide, even if the gelatin contained excess oxygen. Increased confinement caused a considerable decrease in the amount of hydrogen produced. Several hundred % more hydrogen was found in the Bichel gauge tests, with no confinement, than in the Hercules tank. Wide variations in the amounts of carbon dioxide produced in the different types of apparatus were due to the different degrees of confinement, deposition of free carbon and reaction of the sodium oxide produced with the carbon dioxide, the extent depending upon time and intimacy of contact. While very little methane was found in the Bichel gauge appreciable amounts were found in the Crawshaw-Jones device and the Hercules tank, increasing

[20] Taylor and Rinkenbach, *J. Franklin Inst.*, **204**: 369 (1927).
[21] Jones, *Eng. Mining J.*, **122**: 804 (1927).
[22] Wöhler, U.S.P. 1615606 (Jan. 25, 1927).
[23] Jones and Perrott, *Am. Inst. Min. Met. Eng.*, Tech. Pub. no. 102. 1928. 22 p.

with increasing oxygen deficiency of the explosive. Wrappers contribute largely to methane formation. Very small amounts of nitrogen oxides were found in the gases of explosion in the Bichel gauge but appreciable amounts in the Crawshaw-Jones device, the largest quantities from explosives having oxygen balances close to that required for complete combustion. Oxides of nitrogen increased with increasing flame temperatures and increased confinement. Field tests to determine which type of apparatus is best will be made.

Perrott, Tolch and Crawshaw [24] found that the propulsive strength of an explosive is directly proportional to the theoretical "hot volume" over the range of maximum strength. Explosives balanced as to oxygen are not ideal for maximum propulsive strength, the most favorable range being at -8 to -25 grams oxygen balance. An explosive having an oxygen balance of $+15$ was about 40% weaker than one having the most favorable oxygen balance. With 40% gelatins the effect of oxygen balance on propulsive strength is independent of the manner in which this balance may be varied, *i.e.*, whether by changing the proportion of wrapper or by changing the explosive composition. Nearly balanced explosives, or those containing an excess of oxygen, are stronger, weight for weight, when fired with wrapper. The effect of the wrapper on propulsive strength is unimportant if the oxygen balance is less than 5 grams per hundred cc. of explosive exclusive of wrapper. Since the ingredients of the average commercial gelatin dynamite contain an excess of oxygen, all such gelatins are weaker, weight for weight, when fired without wrapper. An explosive packed in $\frac{7}{8}''$ cartridges has a propulsive strength weight for weight greater than the same explosive packed in $1\frac{1}{4}''$ cartridges, provided that the explosive is nearly balanced or contains an excess of oxygen. These small diameters are not recommended because of the more rapid deterioration with age, resulting in a marked decrease in rate of detonation and sensitiveness.

Gardner, Howell and Jones [25] found that, when an explosive is properly detonated in inert rock, the only toxic gas produced in dangerous quantities is carbon monoxide. Only small amounts of sulfur dioxide and nitrogen oxides are formed. In massive sulfide ore dangerous quantities of hydrogen sulfide and sulfur dioxide form. A 40% gelatin dynamite can be manufactured so as to give

[24] Perrott, Tolch and Crawshaw, Am. Inst. Min. Met. Eng., *Tech. Pub.*, no. 101, 1928. 10 p.
[25] Gardner, Howell and Jones, Bur. of Mines, *Bull.* 287, 1927. 96 p.

small amounts of carbon monoxide in the gases from explosion. As regards the amount of carbon monoxide in the gases, the oxygen balance is very important and the age of the explosive also has an effect—old, insensitive explosives giving more carbon monoxide; the use of a larger blasting cap was no improvement. Analysis showed that gases from actual blasting were not always the same as those obtained from a Bichel gauge. Removal of the wrapper from the cartridge reduced the amount of carbon monoxide formed on explosion, but this also reduced the strength. Contrary to previous assumptions that nitrogen oxides are likely to form on blasting with an explosive containing more than 5 to 6% of oxygen, 40% gelatin dynamites containing 3.7 and 5.3% excess oxygen gave no more nitrogen oxides than did gelatins containing an oxygen deficiency. Less carbon monoxide was found in wet than in dry blasting. Although less toxic gases were produced by some explosives than by others, it was shown that with all those tested efficient ventilation was required before return to work. In hard rock the use of stemming reduced the amount of carbon monoxide formed.

An explosive new to the United States, although not at all so to Europe, is pellet powder,[26] or black powder compressed into cylinders having a central perforation placed end to end and wrapped in cartridges. They have various speeds of combustion to suit various conditions. The advantages claimed are greater safety in use, convenience in handling, improved execution, decrease in smoke, improved water resistance and economy.

Ryan and Lantz [27] give a new method of studying the rate of evolution of oxides of nitrogen from nitrocellulose heated to high temperatures. The logarithm of the rate of evolution, plotted against the temperatures, gives a straight line. The stability of the sample examined is largely responsible for the slope of the line. From a determination of the temperature coefficient of the decomposition rate, the stability of the sample at lower temperatures can be estimated. Addition of small amounts of various salts changes the stability.

A rather radical permissible explosive is described by Stoops.[28] By the use of light balsa wood, impregnated with a low-melting point mixture of ammonium nitrate and hydrated magnesium nitrate, he makes an explosive which has about one-half the

[26] duPont Explosives Service Bull., 1927. 8 p.
[27] Ryan and Lantz, *Ind. Eng. Chem.*, **20**: 40 (1928).
[28] Stoops, *Explosives Eng.*, **6**: 174 (1928); U.S.P. 1671792, 1671793 (May 29, 1928).

density of the old type of permissibles, without any of the disadvantages of insensitiveness after subjection to high temperatures. The cushioning effect obtained hitherto only by air-spacing or compressible stemming is now obtained within the cartridge itself because of the great volume of the latter. The high velocity of detonation as compared to black powder is nullified by this cushioning action. A given weight of this explosive is in contact with a greater area of coal, thus reducing still further the shattering action.

Dunn [29] states that about 500,000,000 pounds of explosives were carried by the United States and Canadian railroads in 1927 with no injuries whatever to persons and with a money loss of but $45 in four accidents from fireworks. Flammable liquids and solids, acids and corrosive liquids, compressed gases, etc., caused several deaths and substantial monetary losses.

Routledge [30] advocates replacement of black blasting powder by permissible explosives fired electrically in all bituminous coal mines, and gives examples from experience to support his recommendation.

Jones [31] investigated the flammability of various refrigerants for use in metal mines so deep that artificial cooling will be required if they are driven deeper. Substitution of chlorine or bromine in methane or ethane reduces the flammability. Flammable mixtures of chloromethane or chloroethane and air ignite more readily from a spark than a flame. The upper limits of flammability of such mixtures can be calculated fairly accurately by Le Chatelier's law, but the lower-limit mixtures do not follow the law closely, observed values being about 1% lower. Mixtures of bromo- and chloromethane or chloroethane are flammable with air, but the limits are narrowed by the presence of bromoethane.

As usual, many patents for explosives have been issued. Snelling [32] prepared crystals of ammonium nitrate containing disseminated particles of a sensitizing agent like trinitrotoluene, to which nitrostarch may be added. Bergeim [33] nitrates ethylene oxide mixed with glycol. Segay [34] coats ammonium nitrate with paraffin and adds a perchlorate similarly coated, adding also calcium silicide, etc. Flürscheim [35] makes a waterproof explosive from trinitro-

[29] Dunn, B. E. Rept. no. 21 (Mar. 6, 1928). 65 p.
[30] Routledge, *Mining Congress J.,* 14: 180 (1928).
[31] Jones, *Ind. Eng. Chem.,* 20: 367 (1928).
[32] Snelling, U.S.P. 1617182 (Feb. 8, 1927).
[33] Bergeim, U.S.P. 1637726 (Aug. 2, 1927).
[34] Segay, U.S.P. 1620696 (Mar. 15, 1927).
[35] Flürscheim, U.S.P. 1624401 (Apr. 12, 1927).

aniline, which cannot be fused conveniently, by permeating it with trinitrotoluene. Snelling [36] uses hydrocellulose with nitrostarch, nitroglycerin, trinitrotoluene, etc. Moran [37] nitrates the dextrose-glucoside of glycerol, glycol, etc., in admixture with glycerol or glycol. Bergeim [38] uses triazoethanol nitrate, nitroglycerin, wood meal, calcium carbonate, etc. O'Neil [39] forms globular grains of ammonium nitrate by allowing molten material to solidify as a drop. Symmes [40] does the same thing but obtains solidified drops having an internal void. Davis [41] uses trinitrophenylbutylnitramine in boosters, detonators, cordeau, primers, etc. Swint [42] adds bagasse pith to dynamite to reduce its density. Parodi-Delfino [43] uses phthalide or its homologs as gelatinizing agents for nitrocotton in gelatin dynamite. Moran [44] accelerates gelatinization of nitrocotton by nitroglycerin by adding a small amount of ethyl alcohol or the like.

von Herz [45] uses lead methylene diisonitroamine in blasting caps. Olin, Davis and Smith [46] slit the copper wires of a blasting cap, insert the bridge-wire and mash together instead of soldering. Grant [47] patents methods of short-circuiting exposed ends of electric blasting cap wires to prevent accident explosions. Marshall [48] adds ground corn stalk to dynamite to reduce its density. Rinkenbach [49] reviews the discovery of ethylene glycol dinitrate and the development of methods of producing it and of glycol, showing the physical properties of each. The dinitrate is now used to replace nitropolyglycerin and prevent freezing. Thus the dynamite industry becomes more independent of variations in the price and supply of glycerol. Also he describes [50] the manufacture and properties of diethylene glycol dinitrate. This material is quite insensitive as an explosive but may explode when mixed with nitroglycerin. Champney [51] adds ground oat hulls to permissible explosives to prevent their hardening in warm weather.

[36] Snelling, U.S.P. 1631070 (May 31, 1927).
[37] Moran, U.S.P. 1630577 (May 31, 1927).
[38] Bergeim, U.S.P. 1620715 (Mar. 15, 1927).
[39] O'Neil, U.S.P. 1627863 (May 10, 1927).
[40] Symmes, U.S.P. 1613334 (Jan. 4, 1927).
[41] Davis, U.S.P. 1607059 (Nov. 16, 1926).
[42] Swint, U.S.P. 1609221 (Nov. 30, 1926).
[43] Parodi-Delfino, U.S.P. 1609303 (Dec. 7, 1926).
[44] Moran, U.S.P. 1640712 (Aug. 30, 1927).
[45] von Hertz, U.S.P. 1625966 (Apr. 26, 1927).
[46] Olin, Davis and Smith, U.S.P. 1626118 (Apr. 26, 1927); Olin, 1631756 (June 7, 1927).
[47] Grant, U.S.P. 1606413 to 1606419 (Nov. 9, 1926).
[48] Marshall, U.S.P. 1614447 (Jan. 11, 1927).
[49] Rinkenbach, *Chem. Met. Eng.*, **34**: 296 (1927).
[50] Rinkenbach, *Ind. Eng. Chem.*, **19**: 925 (1927).
[51] Champney, U.S.P. 1650186 (Nov. 22, 1927).

O'Barr [52] waterproofs ammonium nitrate by coating it with tung oil, rosin and paraffin.

F. I. and E. duPont [53] colloid nitrocotton with grains of a mixture of charcoal and a nitrate to make flashless smokeless powder. O'Neil [54] makes a bulk smokeless powder of high-nitrated nitrocotton and dinitrotoluene or dinitrobenzene as a deterrent to reduce speed of burning. Also [55] he forms powder grains of a dense core and a porous envelope, or covers grains of dense, colloided nitrocotton with a surface layer impregnated [56] with oxidizing salts, dinitrotoluene, etc. Olin and O'Neil [57] make a mixture of slow-burning and quick-burning powder grains of the same density. F. I. and E. duPont [58] prepare smokeless powder containing nitrocotton and an explosive such as ammonium nitrate and nitroglycerin, which has a substantially higher oxygen content than the nitrocotton, the grains being perforated to give the powder a density of loading at least 15% less than that for a single base powder. They also [59] incorporate black powder with soluble nitrocotton and colloid with ether-alcohol, or [60] prepare a flashless smokeless powder containing barium and potassium nitrates and soluble nitrocotton colloided by ether-alcohol. Another of their processes [61] is the colloiding of nitrocotton and a small quantity of potassium bichromate and charcoal, or [62] blending nitrocotton with black powder in the presence of alcohol, which does not colloid the nitrocotton but which is useful in the subsequent colloiding after adding ether. Keck [63] makes a smokeless powder containing nitrocotton 74.5, dinitrobenzene 20, mononitroxylene 5, diphenylamine 0.5.

To recover pure nitrocotton from scrap smokeless powder Speicher [64] dissolves in acetone smokeless powder containing diphenylamine, adds toluene, and separates the precipitated nitrocotton. Butts [65] boils smokeless powder containing diphenylamine in isopropyl alcohol, in which the diphenylamine is soluble.

[52] O'Barr, U.S.P. 1648861 (Nov. 8, 1927).
[53] duPont and duPont, U.S.P. 1627639 (May 10, 1927).
[54] O'Neil, U.S.P. 1608808 (Nov. 30, 1926).
[55] O'Neil, U.S.P. 1627861 (May 10, 1927).
[56] O'Neil, U.S.P. 1627862 (May 10, 1927).
[57] Olin and O'Neil, U.S.P. 1627859 (May 10, 1927).
[58] duPont and duPont, U.S.P. 1627691 (May 10, 1927).
[59] duPont and duPont, U.S.P. 1627692 (May 10, 1927).
[60] duPont and duPont, U.S.P. 1627693 (May 10, 1927).
[61] duPont and duPont, U.S.P. 1627694 (May 10, 1927).
[62] duPont and duPont, U.S.P. 1627638 (May 10, 1927).
[63] Keck, U.S.P. 1649784 (Nov. 15, 1927).
[64] Speicher, U.S.P. 1653519 (Dec. 20, 1927).
[65] Butts, U.S.P. 1650689 (Nov. 29, 1927).

Liquid oxygen explosives receive their share of attention. Holderer [66] states that they have been found very efficient and economical in stripping and getting out coal in Indiana. Schultz and Hunter [67] state that at Chuquicamata, Chile, 937,195 tons of rock were broken, and 494,295 pounds of liquid oxygen produced, liquid oxygen explosives at \$0.85 replacing dynamite at \$0.16. Distinct savings were found in shooting this hard rock.

Kostevitch [68] describes how 1,000,000 loaded amatol shell were washed out without accident, also [69] how loaded shell should be burned out.

Hale [70] lists the properties desired, the reason why, and gives experimental determinations of military high explosives. La-Motte [71] reviews the development of nitroglycerin explosives from Nobel's original kieselguhr dynamite to the most recent ammonium nitrate and gelatin dynamites and permissibles, pointing out the differences in materials and technique for smokeless powder *vs.* dynamite, which are so great that it is futile to expect, in time of war, to utilize dynamite plants and their staffs for the manufacture of smokeless powder and that in such times dynamite is needed to an even greater extent to get out other materials.

Munroe [72] defines permissible explosives and recommends adding an age limit to the specifications, due to change of sensitiveness and rate of detonation with time. Pascal [73] relates how 1,200,000 tons of explosives and 300,000 tons of smokeless powder were made in France during the war. Norman [74] patents a method of packing dynamite in freight cars to prevent shifting.

Lanier [75] confines the explosive in a steel tube open at the rear end, so as to apply the full force of the explosion at the back of the bore hole, to obtain a greater proportion of lump coal. An ingenious expanding metal block takes the place of the tamping.

[66] Holderer, *Am. Inst. Mining Met. Eng.*, 1652A-F (preprint, 13 p.), 1927.
[67] Schultz and Hunter, Am. Inst. Mining Met. Eng., *Tech. Pub.* no. 61. 16 p. (1928)
[68] Kostevitch, *Coast Artillery J.*, **65**: 373 (1926).
[69] Kostevich, *Coast Artillery J.*, **65**: 463 (1926).
[70] Hale, *Army Ordnance*, **8**: 115 (1927).
[71] LaMotte, *Army Ordnance*, **7**: 198 (1926).
[72] Munroe, Bur. of Mines, *Informational Circ.* no. 6051 (Nov., 1927).
[73] Pascal, *Army Ordnance*, **8**: 103 (1927).
[74] Norman, U.S.P. 1625491 (Apr. 19, 1927).
[75] Lanier, *Min. Congress J.*, **14**: 456 (1928).

Chapter XLII.

Azo Dyes and Intermediates.

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The small number of published disclosures from the research laboratories of the industries engaged in the manufacture of azo dyes and intermediates is by no means a measure of the amount of research carried on in this field by the industry. Much of this work is necessarily of a confidential nature and relates to reduction of cost, improvement in quality of intermediates or finished dyes, and the development of new products. That this work is extensive is evidenced by the continued reduction in selling prices of dyes, the large number of new colors placed on the market, and the still larger number of older dyes which have been improved in quality.

Judging from the increased number of publications in this field there is much interest shown by American chemists in research work on dyes, intermediates and related organic compounds. In a series of articles, Nicolet and his co-workers [1] discuss "positive" halogens in aromatic compounds. It was found that certain compounds containing bromine or iodine in the benzene ring could undergo hydrolysis in such a way that the halogen was replaced by hydrogen with the liberation of free halogen. Such behavior constitutes the authors' experimental definition of "positive" halogen in organic combination. These papers report the preparation of a number of new iodo derivatives of resorcinol and *m*-phenylenediamine, some new bromo and iodo derivatives of *p*-phenylenediamine, and new halogen derivatives of 2-iodo-4-

[1] Nicolet and Sampey, *J. Am. Chem. Soc.*, **49**: 1796 (1927); Nicolet and Ray, *ibid.*, **49**: 1801 (1927); Nicolet and Sandin, *ibid.*, **49**: 1806 (1927); Nicolet, *ibid.*, **49**: 1810 (1927).

aminotoluene. It was found that the halogen possesses this rela- tively positive character only when in the ortho or para position to an amino or hydroxyl group. A theory to account for the mechanism of the elimination of positive halogen from amino de- rivatives involving the formation of a quinoidal intermediate compound and subsequent 1,3 elimination is suggested.

Two papers by Sampey [2] deal with the development of a quanti- tative method for the determination of the relative rates of acid hydrolysis of positive halogens attached to carbon in certain aromatic compounds and with a study of the kinetics of this reaction.

Three papers by E. Emmet Reid and his co-workers [3] deal with the alkylation of benzene, toluene and naphthalene, and some derivatives of ethylbenzene and of *m*-diethylbenzene. It was found that benzene, toluene and naphthalene could be ethylated by use of ethylene in the presence of aluminum chloride with high speed stirring. Similar results were obtained using propylene. Cyclo- hexene also reacts with benzene under the same conditions. Nitro, amino, hydroxy, halogen amino, sulphoamino and several other derivatives of ethylbenzene and diethylbenzene were prepared. It was found that the isomeric *o*- and *p*-nitroethylbenzenes could be separated by one distillation through a high-precision vacuum still. A number of azo dyes were prepared from some of the amino derivatives of ethylbenzene and *m*-diethylbenzene by diazotizing and coupling with various intermediates such as H-acid, chromo- trope acid, R-salt, J-acid, N & W-acid, Schaeffer's salt, *p*-amino- benzoyl J-acid, Armstrong acid, J-acid urea, etc. These dyes were compared in their dyeing properties with dyes made from aniline and from the corresponding amino derivatives of methylbenzene and of *m*-dimethylbenzene. The dyes prepared from the ethyl derivatives gave similar colors in each case but were deeper in shade than any of the others.

Pinck [4] gives a method for the nitration of organic substances with nitrogen tetroxide in the presence of sulfuric acid. Using benzene, nitrobenzene, toluene and naphthalene as examples, yields of the nitro compounds ranging from 87% to upwards of 90% of the theoretical were obtained. The method involves an inter- mediate reaction of the nitrogen tetroxide with the sulfuric acid,

[2] Sampey, *J. Am. Chem. Soc.*, **49**: 2849, 2853 (1927).
[3] Berry and Reid, *J. Am. Chem. Soc.*, **49**: 3142 (1927); Cline and Reid, *ibid.*, **49**: 3150 (1927); Copenhaver and Reid, *ibid.*, **49**: 3157 (1927).
[4] Pinck, *J. Am. Chem. Soc.*, **49**: 2536 (1927).

whereby nitrating and dehydrating reagents are simultaneously formed.

Further work on nitrations is reported by Bacharach.[5] It is shown that the nitrating action of metallic nitrates on organic compounds is a selective one. The reaction is carried out in glacial acetic acid or acetic anhydride or in both. It was found that compounds like nitrobenzene, benzoic acid, benzaldehyde, etc., were not nitrated by this method, while aromatic amino compounds such as aniline and p-toluidine readily yield nitro bodies. Cupric nitrate is apparently the most active nitrate of the metallic nitrates investigated.

Brown, Etzel and Henke[6] have made a study of catalytic reduction of nitro-organic compounds in the liquid system. It was shown that liquid nitro-compounds and nitro-compounds in suitable solvents, such as benzene and ethyl alcohol, can be reduced quantitatively to amines with hydrogen under pressure and with a nickel catalyst. Nitrobenzene, α-nitronaphthalene, p-nitrotoluene, o-nitrophenol and dinitrobenzene were reduced quantitatively at 215° C. and at a pressure of 500 lbs. per sq. in., using 0.52 gram of nickel catalyst for each gram of nitro-compound reduced.

Two papers by Wheeler and his co-workers report a continuation of p-cymene studies. The first article[7] describes the preparation of p-cymylene-2,5-diamine by coupling diazotized sulfanilic acid to aminocymene and reducing the dye thus formed with stannous chloride. The sulfate of 2-amino-5-bromo-p-cymene was prepared. Some new azo dyes were made by coupling diazotized 2-amino-5-bromo-p-cymene to o-cresol, catechol, phloroglucinol, carvacrol, and p-toluidine. Dyes were also prepared by coupling diazotized sulfanilic acid and diazotized anthranilic acid to the aminobromocymene.

In the second paper[8] 2-amino-5-nitro-p-cymene was obtained by nitration of 2-acetylamino-p-cymene and two new azo dyes were prepared by coupling the diazotized 2-amino-5-nitro-p-cymene to 2-naphthol and to 1-naphthol-4-sulfonic acid.

Bogert and Smidth[9] describe the preparation of 2(m-aminophenyl)-6-methylbenzothiazole and 2(o-aminophenyl)-6-methyl-

[5] Bacharach, *J. Am. Chem. Soc.*, **49**: 1522 (1927).
[6] Brown, Etzel and Henke, *J. Phys. Chem.*, **32**: 631 (1928).
[7] Wheeler and Cutlar, *J. Am. Chem. Soc.*, **49**: 2819 (1927).
[8] Wheeler and Brooke, *J. Am. Chem. Soc.*, **49**: 2832 (1927).
[9] Bogert and Smidth, *J. Am. Chem. Soc.*, **49**: 3135 (1927).

benzothiazole by treating aminothiocresol with *o*- or *m*-nitro-benzoyl chloride and subsequent reduction. The meta isomer on sulfonation and treatment with sodium hypochlorite in caustic solution gave a dye similar to Chloramine Yellow. A similar dye could not be obtained from the ortho derivative.

Lucas and Scudder [10] describe the preparation of 2-bromo-*p*-cresol in yields of 47% from *p*-nitrotoluene by bromination, re-duction, diazotization and replacement of the diazonium group with hydroxyl.

In the manufacture of phenol from sodium benzenesulfonate, the effect of temperature, amount of caustic soda, and length of time of heating upon the yield of phenol were investigated, and the optimum conditions for the fusion were determined by Rhodes, Jayne and Bivins.[11] It was found that if air is allowed to come in contact with the melt some of the phenol is oxidized, and that local deficiency of alkali results in the formation of diphenyl ether and thiophenol, thus decreasing the yield and contaminating the product.

An investigation of hydrolysis of naphthalene-1,5-disulfonic acid has been made by Lynch and Scanlan.[12] Naphthalene-1,5-disulfonic acid, as the free acid, was heated in sealed tubes with concentrations of sulfuric acid ranging from 1% to 85% at tem-peratures ranging from 100° to 220° C. It was found that the 1,5-acid is hydrolyzed to naphthalene when heated with low concentrations of sulfuric acid. In higher concentrations of sul-furic acid it is converted by hydrolysis and resulfonation into those isomeric disulfonic acids which would be obtained by the sulfonation of naphthalene under identical conditions.

Hale and Britton [13] set forth the history and development of the hydrolysis of benzene halides, and describe methods for the commercial manufacture of phenol from chlorobenzene.

May and Hunt [14] have prepared some azo dyes soluble in non-aqueous solvents. These dyes show pronounced solubility in paraffins, aromatic hydrocarbons, linseed oil, carbon tetrachloride, etc. Their solubilities in toluene and in carbon tetrachloride were determined.

Dunning and Reid [15] describe the preparation of a number of

[10] Lucas and Scudder, *J. Am. Chem. Soc.*, **50**: 244 (1928).
[11] Rhodes, Jayne and Bivins, *Ind. Eng. Chem.*, **19**: 804 (1927).
[12] Lynch and Scanlan, *Ind. Eng. Chem.*, **19**: 1010 (1927).
[13] Hale and Britton, *Ind. Eng. Chem.*, **20**: 114 (1928).
[14] May and Hunt, *Ind. Eng. Chem.*, **20**: 384 (1928).
[15] Dunning and Reid, *J. Am. Chem. Soc.*, **49**: 2869 (1927).

azo dyes by coupling diazotized stibanilic acid with various phenols, naphtholsulfonic acids, and aminonaphtholsulfonic acids. These dyes were tested pharmacologically on rats infected with *Trypanosoma equiperdum*. It was found that the dyes prepared from stibanilic acid and phenols and amines of the benzene series were totally ineffective, while those dyes formed from naphthol or aminonaphtholsulfonic acids gave positive results. The dye from stibanilic acid and H-acid proved to be the most effective. A number of these dyes were compared with the corresponding dyes prepared from sulfanilic acid. It was found that the dyes containing antimony were substantive to cotton while the corresponding dyes containing sulfur had no affinity for cotton.

Some interesting work has been done by Weiser and Porter [16] on the physical chemistry of color lake formation. The only azo dyes investigated were Orange II and Metanil Yellow. It was found that lake formation consists in the adsorption of the colored ion by the hydrous oxides. There is no indication of the formation of definite chemical compounds between the dye and the mordant at any hydrogen-ion concentration. The presence of a high concentration of H_2SO_4 in the bath prevents the adsorption of the dye and causes it to be precipitated as the corresponding free acid.

Beattie and Toepler [17] have made a number of azo compounds by coupling various diazo bodies with *o*-cresotinic acid anilide.

Some work has been done at the Bureau of Standards by Appel and Cady [18] on light fastness of various dyes including a number of azo dyes, also a study of the fastness to light of dyestuffs on woolen and worsted fabrics has been made by Barker and others.[19]

Thirty-nine new dyes have been placed on the market by American dye manufacturers during this period. It is estimated that nine of these represent distinctly new chemical individuals. These new colors are to some extent a measure of the amount of research work done by the American dyestuff industry in the various industrial laboratories.

Four U. S. patents on azo dyes have been granted to Americans during this period:

U. S. P. 1,647,145 (Nov. 1, 1927, James P. Penny, National Aniline & Chemical Co.) covers the disazo dyes from β-naphthyl-

[16] Weiser and Porter, *J. Phys. Chem.*, **31**: 1383, 1704 (1927).
[17] Beattie and Toepler, *Am. Dyestuff Rept.*, **16**: 401 (1927).
[18] Appel and Cady, *Am. Dyestuff Rept.*, **16**: 707, 715 (1927); **17**: 15 (1928).
[19] Barker and others, *J. Soc. Dyers Colourists*, **43**: 253, 296 (1927).

aminedisulfonic acids, a primary amine of the benzene series and an *o*-hydroxycarboxylic acid of the benzene series, and the process of making these dyes. The dye from 2-naphthylamine-6,8-disulfonic acid, aniline and salicylic acid gives yellow shades on wool which become orange to brown when after-chromed.

U. S. P. 1,647,162 (Nov. 1, 1927, Henry Wenker, National Aniline & Chemical Co.) covers a composition product containing Cotton Yellow G (diphenylurea-*p,p*-disazobissalicylic acid) with an alkaline substance capable of forming a readily soluble salt. A mixture of the free acid of Cotton Yellow G with disodium phosphate and a calcium oxide free neutral alkali metal salt is characterized by ready solubility in water to form clear solutions in concentrations suitable for dye bath use.

U. S. P. 1,656,233 (Jan. 17, 1928, James P. Penny, National Aniline & Chemical Co.) relates to oil soluble azo dyes obtained by coupling a diazotized aryl amino body with a phenol or naphthol in comixture with hydrolytic decomposition products of a diazo-tized arylamino body. These dyes are suitable for pigments or oil soluble colors.

U. S. P. 1,663,454 (Mar. 20, 1928, Henry Jordan, E. I. duPont deNemours & Co.) covers blue to gray trisazo dyes for cotton and the process of preparing the same. They are made by coup-ling a diazo compound of the benzene or naphthalene series with an α-aminonaphthalene compound, diazotizing the amino azo com-pound thus formed, coupling it to the same or another α-amino-naphthalene compound, then diazotizing the amino disazo body and coupling to acidyl-2-amino-8-naphthol-6-sulfonic acid. The dye prepared from sulfanilic acid, Cleve's acid, α-naphthylamine and acetyl gamma acid gives bluish-gray shades on cotton.

Thirteen U. S. patents have been granted on intermediates for azo dyes:

U. S. P. 1,633,123 (June 21, 1927, Ralph A. Nelson, National Aniline & Chemical Co.) covers a process of producing compounds of the benzidine series from hydrazo compounds, which comprises subjecting a solution of the hydrazo compound in an organic sol-vent immiscible with water to the action of strong hydrochloric acid.

U. S. P. 1,638,045 (Aug. 9, 1927, John W. Livingston and Lucus P. Kyrides) relates to a process of nitrating benzene to form nitrobenzene by the gradual addition of sulfuric acid, ben-

zene and sodium nitrate to a mixture of sulfuric acid, nitro-benzene and benzene heated to a temperature of about the boiling point of benzene.

U. S. P. 1,640,737 (Aug. 30, 1927, Guy B. Taylor and Albert S. Richardson, E. I. duPont deNemours & Co.) covers a process of producing organic nitro compounds by subjecting the organic compound to the action of a nitrating mixture formed by absorbing nitrogen peroxide in concentrated sulfuric acid, which mixture contains substantial proportions of nitric, sulfuric and nitroso-sulfuric acids. The patent also covers the process of denitrating the spent acid to form free nitric oxide, oxidizing the latter to nitrogen peroxide and absorbing this in concentrated sulfuric acid to form a fresh nitrating mixture.

U. S. P. 1,644,483 (Oct. 4, 1927, Ralph A. Nelson and Auton Prasil, National Aniline & Chemical Co.) covers a process of producing and isolating hydrazo compounds, which comprises the reduction of a nitro compound with zinc and caustic alkali in the presence of alcohol, directly distilling off the alcohol at the end of the reduction, and extracting the hydrazo compound from the zinc residue by a solvent immiscible with water.

U. S. P. 1,644,484 (Oct. 4, 1927, Ralph A. Nelson and Auton Prasil, National Aniline & Chemical Co.) covers a process of re-ducing a nitro compound to a hydrazo compound by subjecting the nitro compound, in solution in an organic solvent immiscible with water, to the reducing action of zinc and caustic alkali until the hydrazo stage is reached, the amount of zinc being in excess of that required to form sodium zincate with the caustic alkali.

U. S. P. 1,648,839 (Nov. 8, 1927, W. S. Calcott, A. R. Hitch, and H. W. Mahr, E. I. duPont deNemours & Co.) covers a process of producing 2,3-hydroxynaphthoic acid by heating β-naphtholate in contact with carbon dioxide at a temperature above 180° C. while maintaining the pressure of the carbon dioxide so high as to inhibit decomposition of any alkali metal 2,1-hydroxy-naphthoate formed.

U. S. P. 1,658,230 (Feb. 7, 1928, Chas. R. Downs, Weiss & Downs) covers a process for the fusion of aromatic sulfonates to form aromatic hydroxyl compounds, which consists in heating the alkali metal sulfonate with an alkali metal hydroxide in the proportion of between two and two and one-half molecules of alkali metal hydroxide for each atom of sulfur present in the

alkali metal sulfonate, at a temperature between 300° C. and 425° C. in a thin layer.

U. S. P. 1,662,396 (Mar. 13, 1928, A. E. Parmelee, E. I. duPont deNemours & Co.) covers a process for the preparation of β-naphthol-1-sulfonic acid which consists in sulfonating β-naphthol suspended in nitrobenzene, o-nitrotoluene, benzene, toluene, solvent naphtha or any other suspension medium which is essentially inactive, at a temperature below 16° C. using a solution of sulfur trioxide preferably in the form of fuming sulfuric acid containing 60 to 65% free sulfur trioxide, and separating the β-naphthol-1-sulfonic acid from the inert substance.

U. S. P. 1,663,251 (Mar. 20, 1928, Ivan Gubelmann, H. J. Weiland and Otto Stallmann, Newport Co.) covers a process of separating 3,4-dichloroaniline from a mixture of dichloroanilines which takes advantage of the difference in solubility of the sulfates of these isomeric anilines. The sulfate of 3,4-dichloroaniline is practically insoluble in water.

U. S. P. 1,663,476 (Mar. 20, 1928, Clark W. Davis, E. I. duPont deNemours & Co.) covers a process of producing an aromatic amine by reducing a nitro aromatic compound with iron and water in the presence of sulfuric acid and an alkali metal chloride.

U. S. P. 1,665,005 (Apr. 3, 1928, H. J. Weiland and Ivan Gubelmann, Newport Co.) covers a process for purifying technical m-dinitrobenzene containing other isomers by treating the mixture with a caustic alkali solution of less than 10% strength, whereby the isomeric dinitrobenzenes are converted into water soluble bodies, and separating the water solution of these bodies from the m-dinitrobenzene.

U. S. P. 1,667,480 (Apr. 24, 1928, Vaman R. Kokatnur) covers a method for making alkali fusions of organic compounds, whereby the compound is fused with alkali in the presence of an inert diluent, the amount of alkali introduced being less than about twice the amount required by theory and the inert diluent being one which boils substantially at the temperature at which the reaction effectively takes place. The process is applicable to the preparation of phenols from aromatic sulfonic acids and to the preparation of amino compounds from chloro-aromatic bodies, in which case sodamide is used in place of caustic.

U. S. P. 1,670,406 (May 22, 1928, Ivan Gubelmann and J. M. Linker, Newport Co.) covers a process of preparing H-acid which

consists in fusing 1-naphthylamine-3,6,8-trisulfonic acid with caustic alkalies in the presence of added ammonia.

Correction: In Volume II of the Annual Survey, page 372, the eighth line of the second paragraph should read "by Holmes of the Bureau of Chemistry and Soils of the U. S. Department of Agriculture."

Chapter XLIII.

Anthraquinone Dyes and Intermediates.

Ivan Gubelmann,

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It is rather difficult to fully describe the progress made by American dye producers in the field of anthraquinone dyes and intermediates during the past year. To those familiar with the products of this series, which have been announced by American manufacturers as their first production, it is evident that a great deal of work has been done which is not recorded anywhere in the chemical literature. In addition to a number of anthraquinone colors which have been produced in America for the first time during the past year, there has been a marked improvement in the quality of products formerly produced, which, in many instances, now surpasses that of the imported article. The past year has been a busy one for the printers and consequently there has been a great demand for anthraquinone vat dyes suitable for printing. To obtain the maximum tinctorial value in printing vat colors for a given tinctorial value obtained in dyeing, is a manufacturing problem as well as an application problem. The manufacture of good printing pastes requires, in many instances, special treatment which sometimes calls for a great deal of experimental work.

A further reduction in prices of anthraquinone vat dyes has gone into effect during the past year. This was made possible through the continuous efforts of the laboratories to improve manufacturing methods. Lower costs have also been made possible on account of the increased production, necessitated by the insistent greater demand of the public for faster dyed fabrics. According to the Tariff Commission's advance report,[1] 4,500,000 lbs. of vat dyes were produced during 1927, as compared with

[1] *Am. Dyestuff Rep.*, **17**: 244 (1928).

4,000,000 lbs. during 1926. These figures include all vat dyes with the exception of indigo, and it is believed that most of this increase is probably due to greater production of anthraquinone vat dyes. The total imports of all classes of dyestuffs in 1927 were 16.5% less in value than those in 1926 and it is fair to assume that a substantial percentage of this decrease is due to increased domestic production of anthraquinone dyes.

No reliable figures for the domestic production of acid anthra- quinone (acid alizarine) colors are available, but the total is of course very much smaller than for anthraquinone vat colors. Many dyes are marketed under the name "Alizarine" which are not anthraquinone derivatives.

The consumption and production of the various types of Alizarine Reds continue to be small in comparison with the im- portance of these products in Europe, where Alizarine Reds are made on a very large scale. A large part of the European pro- duction is exported to India, China and other countries.

During the period July 1, 1927, to July 1, 1928, the following anthraquinone dyes have been announced by American manu- facturers as *their* first production:

Anthraquinone Acid Dyes

Acid Anthraquinone Blue S K Y.............	(Newport)
Acid Anthraquinone Green G	(Newport)
Acid Anthraquinone Violet R	(Newport)
Alizarine Cyanone Green G Extra............	(National)
Anthraquinone Violet B, BB, 3R............	(The Synthesis Co.)

Anthraquinone Vat Dyes

Anthrene Blue R C X......................	(Newport)
Anthrene Bordeaux B	(Newport)
Anthrene Brilliant Blue R..................	(Newport)
Anthrene Brown R A......................	(Newport)
Anthrene Orange R C......................	(Newport)
Anthrene Yellow .A G.....................	(Newport)
Carbanthrene Black B Double Paste..........	(National)
Carbanthrene Blue G C D Double Paste......	(National)
Carbanthrene Yellow G Double Paste........	(National)
Hydroform Black G, GB, G2B...............	(Peerless)
Hydroform Deep Blue R O..................	(Peerless)
Hydroform Bright Yellow 3 G...............	(Peerless)
Indanthrene Brown R A....................	(General Dyestuff Corp.)
Ponsol Blue G Z Double Paste...............	(duPont)
Ponsol Brown A R Double Paste............	(duPont)
Ponsol Yellow A R Double Paste............	(duPont)
Leucosol Black B B........................	(duPont)
Leucosol Blue G	(duPont)
Leucosol Navy Blue B B....................	(duPont)

Of a total of twenty-four dyes announced by various companies as their first production, probably seven have not been made by American manufacturers prior to July 1, 1927, and are to be regarded as distinctly new additions to the line of American-made anthraquinone dyes.

The others are either duplicates or variations of dyes which were manufactured here before July 1, 1927. Among the distinctly new American productions for the period is included the anthraquinone vat dyestuff formerly imported under the name of "Algol Brown R," which is now being made by three American dye producers. This vat dye produces probably the fastest of the known brown shades and its manufacture involves the production of a great many intermediates.

Just about eight years ago the first anthraquinone dye was made commercially in America. Since that time one product after another has been added, until today the textile industry is not absolutely but practically independent of foreign sources of supply. With the present rate of development continued, the industry will in a very short time offer a complete line of anthraquinone dyes. In no other field of organic chemistry is the literature any more incomplete and inaccurate than in the field of anthraquinone chemistry. The industry depended and still depends mostly on information contained in patents, which are too often drawn up with the idea of disclosing as little as possible. For this reason many methods had to be "re-invented" and "the good sifted out from the bad." It is natural, therefore, that little time was spent in new fields with the purpose of inventing new anthraquinone dyes. This condition is reflected by the subjects contained in patents granted to American companies. However, there are now indications that the American companies have at least made a start with original research. The universities have also started to interest themselves in the field of anthraquinone research, and it is hoped that valuable results will come from that source, since the subject is a most interesting one.

Anthraquinone Intermediates. A patent assigned to The Barrett Company [2] discloses an improvement in the oxidation of anthracene to anthraquinone in the vapor phase. The new feature of this method consists in the choice of a catalyst with the purpose of reducing the amount of undesirable by-products to a minimum. A combination of the oxides of two metals, such as

[2] Craver, U.S.P. 1636856 (July 26, 1927).

uranium and molybdenum, but with uranium predominating, is stated to give a yield of about eighty-five pounds of anthraquinone from one hundred pounds of anthracene. The reaction is carried out at a temperature of about 475° C. and the time allowed for the contact of the mixture of anthracene vapor and oxygen-containing gas with the catalyst is about 0.5 second.

A patent has been granted to the National Aniline & Chemical Company [3] for the sublimation of anthracene, anthraquinone, etc. The method is stated to permit semi-continuous operation and consists in charging the finely divided material into an agitated, jacketed receptacle, heating and agitating it until it becomes plastic and then passing superheated steam or hot gases through the receptacle, thereby effecting the sublimation. The condensation of the escaping vapors is accomplished in a water spray condenser. The residue, consisting of non-sublimable material, is removed through a bottom outlet.

Grosvenor [4] describes the preparation of anthraquinone paste, containing about 80% water, which will not show any substantial separation of water on standing.

A patent granted to the National Aniline & Chemical Company [5] describes a modification of a known method for the conversion of anthraquinonesulfonic acids into the corresponding aminoanthraquinone bodies. According to this method an anthraquinonesulfonic acid or its salt is heated with aqueous ammonia in the presence of an organic nitro body and an ammonium salt. 2-Aminoanthraquinone, for example, is made from Silversalt, using ammonium chloride and nitrobenzene in addition to aqueous ammonia. High yields are claimed as the chief advantage of this method.

Stouder and Adams [6] have prepared 1-methyl-2,4-dichloro-anthraquinone by heating 2,4-dichloro-5-methylbenzoyl-*o*-benzoic acid with boric acid and concentrated sulfuric acid. By heating 1-methyl-2,4-dichloroanthraquinone with sodium methylate they obtained 1-methyl-2,4-dimethoxyanthraquinone. By treating this compound with hydrobromic acid 1-methyl-2,4-dihydroxyanthraquinone was obtained, which, with acetic anhydride, gave 1-methyl-2,4-diacetoxyanthraquinone. The synthesis of 1-methyl-2,4-dihydroxyanthraquinone was undertaken with the object of

[3] Field, U.S.P. 1662056 (March 13, 1928).
[4] Grosvenor and Gershon, U.S.P. 1631589 (June 7, 1927).
[5] Rogers, U.S.P. 1644494 (Oct. 4, 1927).
[6] Stouder and Adams, *J. Am. Chem. Soc.*, **49**: 2043 (1927).

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preparing rubiadin, which is one of the pigments of madder.
1-Methyl-2,4-dihydroxyanthraquinone has been shown not to be
identical with rubiadin.

A process for the preparation of 2(or 3)-chloroquinizarine
(2-chloro-1,4-dihydroxyanthraquinone) has been patented by the
Newport Company.[7] The method consists of condensing phthalic
anhydride with 3,4-dichlorophenol in the presence of concentrated
or fuming sulfuric acid and boric acid. A product of exceptional
purity is obtained, which, according to the author's findings, could
not be equalled by chlorinating quinizarine. 2-Chloroquinizarine
is used in the manufacture of acid anthraquinone colors.

The laboratories of the Newport Company [8] have also found
that leucoquinizarine can be prepared from 2-chloroquinizarine, by
adding to a sulfuric acid solution thereof a finely divided metal
powder. The nascent hydrogen generated in this reaction mixture
reduces the quinizarine to the leuco compound and simultaneously
eliminates the chlorine atom, a hydrogen atom replacing the chlo-
rine atom. The reaction mixture obtained by the condensation of
phthalic anhydride with 3,4-dichlorophenol in the presence of
concentrated sulfuric acid and boric acid can be used directly for
the preparation of leucoquinizarine.

A patent granted to the Newport Company [9] describes a novel
method of making 1,3-diamino-2-hydroxyanthraquinone. 3',5'-
Diamino-4'-hydroxy-o-benzoylbenzoic acid is heated with concen-
trated sulfuric acid to a temperature of 175-185° C. After the ring
closing has been completed, the mass is diluted with water and
the end-product thereby precipitated.

The following is an account of work done on anthraquinone
intermediates in foreign laboratories, which is on record either in
U. S. patents or in American periodicals :

Monobenzoyldiaminoanthraquinones have been prepared by the
British Dyestuffs Corporation, Ltd.[10] by heating a benzoic acid
anhydride with a diaminoanthraquinone in the presence of a sol-
vent, such as nitrobenzene.

A patent assigned to Grasselli Dyestuff Corporation [11] describes
a method for the replacement of sulfonic groups in anthraquinone-
sulfonic acids and derivatives with a hydrogen atom. p,p-Diamino-
anthrarufinsulfonic acid, for example, is dissolved in water;

[7] Gubelmann, U.S.P. 1655863 (Jan. 10, 1928).
[8] Gubelmann and Lee, U.S.P. 1655462 (Jan. 10, 1928).
[9] Gubelmann, Weiland and Stallmann, U.S.P. 1659360 (Feb. 14, 1928).
[10] Perkin and Bunbury, U.S.P. 1660090 (Feb. 21, 1928).
[11] Schmidt, U.S.P. 1650158 (Nov. 22, 1927).

pyridine and a hydrosulfite are added and the mixture heated. A colorless precipitate separates out which was found to be practically pure *p,p*-diaminoanthrarufin.

The Scottish-Dyes, Ltd.,[12] has prepared 1-aminoanthraquinone by heating under pressure 1-chloroanthraquinone and ammonia in the presence of a copper catalyst.

A process patent assigned to the British Dyestuffs Corporation, Ltd.,[13] describes a method for the preparation of *N*-methyl-*ω*-sulfonic acids of diaminoanthraquinones, especially the 1,4-diaminoanthraquinone.

Fierz-David[14] states that 13% yield of 1,2-dichloroanthraquinone and 87% yield of 2,3-dichloroanthraquinone are obtained by condensing 3′,4′-dichloro-2-benzoylbenzoic acid in the presence of concentrated sulfuric acid.

Anthraquinone nitrosamine compounds are described in a patent assigned to Grasselli Dyestuff Corporation.[15] These are formed by the action of a nitrous acid compound upon an *N*-substituted aminoanthraquinone compound in the presence of a solvent at a temperature below 40° C. The new compounds are of the general

formula $C_{14}H_7O_2-N\begin{subarray}{l} \diagup NO \\ \diagdown R \end{subarray}$, in which R is an alkyl, aralkyl, or

aryl radical.

A process and product patent assigned to the Grasselli Dyestuff Corporation[16] describes the preparation of Bz-1-benzanthrone-sulfinic acid, by treating a Bz-1-halogen-benzanthrone with hydrosulfite in the presence of ammonia.

2,Bz-1-dibenzanthronyls are described in a patent granted to the I. G.[17] They are obtained by condensing a benzanthrone with free 2- and Bz-1-positions with a Bz-1-halogen-benzanthrone with a free 2-position by means of an alkaline condensing agent. 2,Bz-1-dibenzanthronyls are stated to yield pure isodibenzanthrones, which have heretofore been made by fusing chlorobenzanthrones with alcoholic caustic alkali.

Anthraquinone Acid Dyes. There is no evidence that there has been great activity in research in the field of anthraquinone acid dyes in the past year, either here or abroad.

[12] Thomas and Davies, U.S.P. 1657420 (Jan. 24, 1928).
[13] Perkin, Fyfe and Mendoza, U.S.P. 1636485 (July 19, 1927).
[14] Fierz-David, *J. Am. Chem. Soc.*, **49:** 2334 (1927).
[15] Tesche and Job, U.S.P. 1643428 (Sept. 27, 1927).
[16] Neresheimer and Emmer, U.S.P. 1644851 (Oct. 11, 1927).
[17] Luettringhaus, Neresheimer and Wolff, U.S.P. 1633866 (June 28, 1927).

According to a patent assigned to Grasselli Dyestuff Corporation,[18] new derivatives of p,p-diaminoanthrarufin-2,6-disulfonic acid (Saphirol B) may be obtained by preparing the boric acid ester in concentrated sulfuric acid solution and adding a phenol. A product of addition is formed which rearranges itself to form 1,5-dihydroxy-4,8-diamino-2-hydroxyphenyl-6-anthraquinone sulfonic acid. It is stated that this compound dyes unmordanted wool from an acid bath beautiful blue shades of excellent fastness to perspiration and alkalies.

Anthraquinone Vat Colors. One of the most important vat dyes is N-dihydro-1,2,2′,1′-anthraquinoneazine and its halogen derivatives. During the period four patents which deal with these products have been granted to American dyestuff manufacturers.

The laboratories of the duPont Company [19] worked out a new method for the chlorination of N-dihydro-1,2,2′,1′-anthraquinoneazine, which seems to be especially adapted for the preparation of polychloro-derivatives. The starting material is suspended in acetic acid or in a mixture of acetic acid and nitrobenzene and chlorine gas passed through the suspension at temperatures varying between 40-115° C. The chlorine content of the finished product may be varied considerably, depending on manipulation. Greener shades and greater fastness to chlorine bleach are stated to be the main advantages of the method in comparison with methods previously described.

A patent granted to the National Aniline & Chemical Company [20] describes a method for the halogenation of anthraquinone derivatives, particularly vat coloring matters of the benzanthrone-, pyranthrone-, and indanthrone-series. According to this patent the starting material is dissolved or suspended in a suitable solvent and heated with chlorine, bromine, etc., in the presence of sulfur dioxide. In this manner a similar effect is obtained with chlorine as by the use of sulfuryl chloride as chlorinating agent, which is known to be valuable if destruction of material through oxidation by the free halogen is to be avoided.

A method for the preparation of N-dihydro-1,2,2′,1′-anthraquinoneazine from the halogenated azines has been found by the Newport Company laboratories.[21] It consists in heating a halogenated azine with a suitable dehalogenizing agent, capable of

18 Schmidt, U.S.P. 1652584 (Dec. 13, 1927).
19 Bishop, U.S.P. 1637851 (Aug. 2, 1927).
20 Crowell, U.S.P. 1646235 (Oct. 18, 1927).
21 Ulich and Goodrich, U.S.P. 1634473 (July 5, 1927).

replacing the halogen atoms by hydrogen atoms. Alcoholic potash was found to be an effective dehalogenizing agent.

A process and product patent granted to the duPont Company [22] describes the preparation of N-dihydrodianthraquinone-azine suitable for the use as pigment. The leuco derivative of the azine is suspended in a large quantity of water and oxidized by blowing air through the agitated mass at a temperature of about 100° C. The product is obtained in form of fine hair-like crystals and is stated to possess excellent properties as a pigment, the shade being greener and brighter than that of products obtained by heretofore known methods.

During the past year the foreign laboratories have obtained patent protection on a number of new vat dyestuffs. They have continued to concentrate on dyestuffs of the benzanthrone series, which have become increasingly important since it was discovered that the ethers of dihydroxydibenzanthrones have unusual properties.

A patent granted to the I. G.[23] describes the preparation of new dyestuffs of the benzanthrone series, which dye cotton from a pure blue hydrosulfite vat in bright greenish-blue shades. They are obtained by condensing ethers of hydroxybenzanthrones which are halogenated in the Bz-1-position and which have a free 2-position, in the presence of an alkaline condensing agent. A specific example describes the dyestuff obtained from Bz-1-chloro-Bz-2-methoxybenzanthrone.

New vat dyes of the isodibenzanthrone series are described in a patent assigned to Grasselli Dyestuff Corporation.[24] These dye-stuffs dye cotton from a blue hydrosulfite vat, pure bluish-violet shades, and are prepared by heating unsymmetrically substituted Bz-1,Bz-1'-benzanthronyl sulfides, having free 2-positions, in the presence of alkaline condensing agents.

The Society of Chemical Industry in Basle [25] has obtained protection on a process, by which part of the halogen of poly-halogenated isoviolanthrones may be eliminated by the treatment of the leuco compounds with alkali and reducing agents. An increased brilliancy of shade is stated to be the result.

According to a patent assigned to the Grasselli Dyestuff Corporation,[26] isodibenzanthrones may be prepared by heating a

[22] Sachs, U.S.P. 1640724 (Aug. 30, 1927).
[23] Nawiasky, Zahn and Saurwein, U.S.P. 1633997 (June 28, 1927).
[24] Nawiasky, Braunsdorf and Holzapfel, U.S.P. 1644849 (Oct. 11, 1927).
[25] Mayer and Siebenbuerger, U.S.P. 1658003 (Jan. 31, 1928).
[26] Neresheimer, U.S.P. 1644850 (Oct. 11, 1927).

mixture of about molecular proportions of a benzanthrone-Bz-1-thio ether and a benzanthrone, both having a free 2-position, with alkaline condensing agents in the absence of oxygen.

Another problem of anthraquinone chemistry to which the foreign laboratories have given much attention, is the production of water-soluble vat dyes.

The Scottish-Dyes, Ltd.,[27] has prepared derivatives of flavanthrone, dimethoxydibenzanthrone, indanthrone and indigo by letting act upon them alkyl esters of chloroacetic acid in the presence of pyridine and either copper or zinc. The end-products are water-soluble dyestuffs which can be used for the dyeing of textiles. The dyeings are after treated with an oxidizing agent such as ferric chloride, which produces the same shade as the original vat dyestuff when dyed from a hydrosulfite vat. The new dyestuffs may also be used for printing.

A patent assigned to Durand and Huguenin [28] describes the preparation of stable water-soluble vat dyestuffs, obtained by heating the leuco compound of the vat dyestuff with aminosulfonic acid in the presence of a tertiary organic base, preferably pyridine.

A number of patents disclose the constitution and method of preparation of new dyestuffs which dye cotton in yellow, orange and brown shades.

A patent assigned to Grasselli Dyestuff Corporation [29] describes new dyestuffs, which produce yellow to orange to red shades on vegetable fibers when dyed from the bluish colored vat. They are of the following type : X—A—NH—R—NH—A—Y, in which X stands for an aroylamino group (for instance, benzoylamino), Y stands for an aroylamino group or hydrogen, R stands for the radical of a dibasic acid (oxalic acid, for instance) and A stands for anthraquinone. One member of this group is prepared by nitrating dianthraquinonyl-1,1'-oxamide and reducing the 4,4'-dinitro compound. The 4,4'-diamino body is finally benzoylated in nitrobenzene solution.

A patent assigned to Grasselli Dyestuff Corporation [30] discloses a method for the preparation of new vat dyes, consisting in the treatment with concentrated sulfuric acid of benzoylated aminoanthrimides. 5,5'-Dibenzoylamino-1,1'-anthrimide, for instance, yields a yellow dyestuff by this treatment, which dyes cotton bright

[27] Wylam, Harris and Thomas, U.S.P. 1640018 (Aug. 23, 1927).
[28] Wolfram, U.S.P. 1639206 (Aug. 16, 1927).
[29] Kugel, U.S.P. 1651461 (Dec. 6, 1927).
[30] Gassner, U.S.P. 1667848 (May 1, 1928).

yellowish orange shades from the alkaline hydrosulfite vat, which are stated to be fast to light and washing.

A patent assigned to Grasselli Dyestuff Corporation [31] describes new dyestuffs which are obtained by condensing anthrones with a glyoxal compound in presence of an acidic substance. After forming the vats these glyoxal-dianthraquinones dye cotton fast clear yellow shades.

The laboratories of the Society of Chemical Industry in Basle [32] have found that the dyestuffs described in U. S. patents 1,437,783, 1,523,308 and 1,568,627, which are triazine bodies obtained by condensing amino-anthraquinones with cyanuric chloride, successfully withstand hypochlorite solutions. The treated dyestuffs produce brighter shades and have better fastness properties.

The laboratories of the British Dyestuffs Corporation, Ltd., [33] have prepared acylaminoflavanthrones by treating flavanthrone with hydroxylamine and acylating the resulting aminoflavanthrone. The benzoylaminoflavanthrone is stated to dye cotton a brown shade.

In conclusion I wish to thank Dr. H. J. Weiland for his assistance in collecting the data for this chapter.

[31] Berliner, Stein and Trautner, U.S.P. 1646782 (Oct. 25, 1927).
[32] Ackermann, U.S.P. 1663474 (Mar. 20, 1928).
[33] Thornley, U.S.P. 1662872 (Mar. 20, 1928).

Chapter XLIV.

Paint and Varnish.*

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The activity of American chemists in problems relating to the paint and varnish industry is shown not only by the large number of papers published but by the great interest shown at the meetings of the Division of Paint and Varnish Chemistry of the American Chemical Society, Committee D-1 on Protective Coatings for Structural Materials of the American Society for Testing Materials and of the various local plant superintendents and production managers' clubs.

The American Society for Testing Materials has issued standard methods of test for specific gravity of pigments,[1] analysis of white pigments,[2] dry red lead,[3] yellow, orange, red, and brown pigments containing iron and manganese,[4] yellow and orange pigments containing chromium compounds, blue pigments and chrome green[5] and titanium pigments.[6] These methods have been most carefully prepared and are the best available for the purposes indicated. The same society has issued standard specifications for ocher,[7] mineral iron oxide,[8] chrome yellow,[9] pure chrome green[10] and reduced chrome green,[11] and tentative specifications for prussian blue,[12] ultramarine blue,[13] chrome oxide green,[14] commercial

* Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.
[1] Am. Soc. Testing Materials Standards, 1927, Pt. II: 277.
[2] Am. Soc. Testing Materials Standards, 1927, Pt. II: 305.
[3] Am. Soc. Testing Materials Standards, 1927, Pt. II: 316.
[4] Am. Soc. Testing Materials Standards, 1927, Pt. II: 321.
[5] Am. Soc. Testing Materials Standards, 1927, Pt. II: 328.
[6] Am. Soc. Testing Materials Standards, 1927, Pt. II: 341.
[7] Am. Soc. Testing Materials Standards, 1927, Pt. II: 255.
[8] Am. Soc. Testing Materials Standards, 1927, Pt. II: 253.
[9] Am. Soc. Testing Materials Standards, 1927, Pt. II: 263.
[10] Am. Soc. Testing Materials Standards, 1927, Pt. II: 265.
[11] Am. Soc. Testing Materials Standards, 1927, Pt. II: 267.
[12] *Proc. Am. Soc. Testing Materials,* **27,** Pt. 1: 850 (1927).
[13] *Proc. Am. Soc. Testing Materials,* **27,** Pt. I: 852 (1927).
[14] *Proc. Am. Soc. Testing Materials,* **27,** Pt. I: 854 (1927).

para red,[15] titanium barium pigment,[16] aluminum powder for paints [17] and gold bronze powder.[18]

Pickard [19] continued his series of articles on pigments, discussing in the period covered by this review a number of the natural mineral pigments.

Nelson and Norris [20] discuss particle size, oil absorption, suspension, hiding power, tinting strength, photochemical stability, chemical reactivity, solubility and ultraviolet transmission of a number of the most important pigments, with particular reference to their use in pigmented lacquers.

Hallett [21] discusses titanium pigment. Fasig and Purdy [22] report experiments on the effect of pigments in the presence of water on inhibition and stimulation of rusting, but fail to call attention to similar work done years ago by the American Society for Testing Materials. Probeck and Battle [23] discuss the action of pigments in primers for metals. While disclaiming any complete study of pigments for this purpose, they find high purity iron oxide one of the best, it being superior to chrome green, chrome yellow and some of the commonly used white pigments. They suggest that a lacquer primer should contain at least 39% of pigment to give proper durability to the entire lacquer system. Mowen [24] discusses the grinding of pigments for lacquers. Lacquer enamels require more finely divided pigments than oleoresinous enamels. He recommends formulas for pebble and buhr mill grinding liquids and gives amounts of a number of pigments which may be ground in a gallon of the liquids recommended.

Bunce [25] gives the ultraviolet transmission of various white pigments and discusses the advantages of zinc oxide as a pigment. Morris [26] claims that lithopone paints are as durable as other white paints and gives a method of testing texture by rubbing the pigment with a good dispersing varnish, spreading on glass, scraping the wet film with a 3-inch putty knife, one side of which rests

[15] *Proc. Am. Soc. Testing Materials,* **27**, Pt. I: 856 (1927).
[16] *Proc. Am. Soc. Testing Materials,* **27**, Pt. I: 858 (1927).
[17] *Proc. Am. Soc. Testing Materials,* **27**, Pt. I: 860 (1927).
[18] *Proc. Am. Soc. Testing Materials,* **27**, Pt. I: 860 (1927).
[19] Pickard, *Am. Paint J.,* **11**: nos. 37, 39, 40, 41, 43, 44, 45, 46, 48, 49, 51 (1927); **12**: nos. 1, 5, 6, 7, 8, 10, 12, 14, 16, 20, 23, 26 (1928).
[20] Nelson and Norris, *Research Bull.,* New Jersey Zinc Co., Sept., 1927.
[21] Hallett, *Am. Paint J.,* **12**: no. 10: 20 (1928). *Also* Official Digest Federal Paint Varnish Producers Clubs, Dec., 1927.
[22] Fasig and Purdy, *Am. Paint Varnish Mfrs. Assoc. Circ.* **319**: 611 (1927).
[23] Probeck and Battle, *Ind. Eng. Chem.,* **20**: 197 (1928).
[24] Mowen, *Paint, Oil Chem. Rev.,* **85**, no. 7: 10 (Feb. 16, 1928).
[25] Bunce, *Am. Paint Varnish Mfrs. Assoc. Circ.* **319**: 541 (1927).
[26] Morris, *Paint, Oil Chem. Rev.,* **85**, no. 5: 10, 19 (Feb. 2, 1928).

on a piece of steel 0.003 inch thick and the other edge on the glass plate. By examining the wedge-shaped film information as to texture is obtained.

Glaze [27] gives a rapid method for analysis of basic lead carbonate. Gardner [28] gives qualitative tests for graphite, boneblack, lampblack, carbon black and black magnetic iron oxide and discusses their possible separation by flotation. Bonner and Kaura [29] determine metallic copper when mixed with cuprous and cupric oxides by treating with NaCN solution which rapidly dissolves Cu_2O and CuO but dissolves Cu slowly.

Committee D-1 of the American Society for Testing Materials has collected valuable information on the characteristics of the raw linseed oil which is sold in America [30] and has issued standard specifications for raw linseed oil [31] of two types (low and high iodine number) and tentative specifications for boiled linseed oil [32] of two types (high and low viscosity). The coöperation of this committee with the Federal Specifications Board has at last re- sulted in agreement as to specifications for raw and boiled linseed oil, and the latest revisions of Federal Specifications Board specifications [33] are in essential agreement with the specifications of the American Society for Testing Materials. Eastman and Taylor [34] state that commercial raw linseed oil is generally crushed from seed that contain "dockage," such as small oleaginous seeds, and show that variation may be expected in oils made from the same crop in the same district if greater or less amounts of "dockage" seeds are allowed to remain mixed with the flaxseed at the time of crushing. They further show that these variations not only affect the so-called constants of the raw oils, but that the differences are maintained in the refined oils made from them and are often magnified in later blowing and heat treatment.

Long, Egge and Wetterau [35] prepare relatively pure linolenic glyceride from perilla and linseed oils. This glyceride when heated at 225° C. seems to undergo an isomeric change. At 250° C. coupling and condensation reactions occur. At 293° it is rapidly decomposed. Blowing favors reactions which decrease the un-

[27] Glaze, *Paint, Oil Chem. Rev.*, **84**, no. 12: 13 (Sept. 22, 1927).
[28] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **323**: 163 (1928).
[29] Bonner and Kaura, *Ind. Eng. Chem.*, **19**: 1288 (1927).
[30] *Proc. Am. Soc. Testing Materials*, **27**, Pt. I: 400 (1927).
[31] Am. Soc. Testing Materials Standards, 1927, Pt. II: 226.
[32] *Proc. Am. Soc. Testing Materials*, **27**, Pt. I: 846 (1927).
[33] U.S. Govt. Master Spec. for Oil, Linseed, Raw, F.S.B. Spec. no. 4a; U.S. Govt. Master Spec. for Oil, Linseed, Boiled, F.S.B. Spec. no. 475a.
[34] Eastman and Taylor, *Ind. Eng. Chem.*, **19**: 896 (1927).
[35] Long, Egge and Wetterau, *Ind. Eng. Chem.*, **19**: 903 (1927).

saturation with relatively small attendant increase in molecular weight. Heating favors coupling and condensation reactions.

Knauss and Smull [36] find that the rate of bromination of oleic, linolic and linolenic acids is in inverse ratio to the number of double bonds; that is, oleic acid reacts most and linolenic acid least rapidly. The rate of bromination of the mixed fatty acids of poppy seed, soya bean, linseed and perilla oils is in direct relation to the acid constituents. Under the influence of ultraviolet light the bromination of both the so-called pure acids and the mixed fatty acids proceeds beyond the bromination in the dark, which indicates the presence of unsaturated isomers which are not shown by present methods of analysis. The authors are convinced that linolenic acid is present in linseed oil in several stereoisomeric forms, so that an explanation of the erratic action of the fatty acids of drying oils may be found from a stereochemical consideration of this problem.

Stutz [37] finds that raw linseed oil films are more transparent to ultraviolet light than films from heat-bodied oil, and films of heavy-bodied air-blown oils are still more opaque. On exposure to the mercury arc or to sunlight, a film of raw linseed oil becomes more transparent (bleaches). A film of air-blown oil also bleaches, though not so much as a raw oil film. A heat-bodied oil film shows but little change and may even become more opaque on exposure to ultraviolet light. Perilla and tung oils become more transparent on exposure to ultraviolet light. Poppy and soya bean oils become more opaque in the near ultraviolet and more transparent in the far ultraviolet. All oil varnishes measured were quite opaque and on exposure to ultraviolet light became more opaque (yellow). The tendency to yellow is least with long oil varnish high in linseed oil and is greatest with short oil varnish high in tung oil. Apparently the resins present are largely responsible for the yellowing of the varnish as well as its high opacity. Clear nitrocotton is quite transparent; the addition of a plasticizer renders it more opaque and the addition of resins renders it still more opaque. Practically all vehicles have high absorption in the short wave lengths beyond the limits of the sun's spectrum. Exposure to such rays therefore accelerates decomposition. On the contrary when exposed to sunlight the radiation, being above 2900 Å, is sometimes able to penetrate a considerable distance into the film before being com-

[36] Knauss and Smull, *J. Am. Chem. Soc.*, **49**: 2808 (1927).
[37] Stutz, *Ind. Eng. Chem.*, **19**: 897 (1927).

pletely absorbed. This difference should be considered in interpreting accelerated weathering tests, when the light source used is rich in waves shorter than those found in sunlight.

Gardner and Levy,[38] in limited tests, find that ultraviolet light produced irregular changes in acid number, iodine number and drying time of linseed oil mixed with various pigments. Long and Moore [39] expose raw and treated linseed, perilla and tung oils for various short periods to cathode rays. This treatment increases the refractive index of all samples of linseed and perilla oils and decreases it in tung oil. The molecular weight increases in all cases, being greatest with samples having initially high molecular weights. With raw linseed oils a sharp drop in hexabromide number before any change in iodine number seems to indicate a change of the linolenic glyceride to an isomer which does not yield a solid hexabromide. In all cases the oils were bleached by the rays and the time of drying was decreased.

Long [40] gives a brief résumé of the fundamental work on drying oils that he and his assistants have been doing for several years. When oil is boiled, at least four major types of reactions occur, oxidation, condensation, coupling at double bonds and isomeric changes. That this fundamental work is appreciated by the industry is evidenced by the fact that, largely from support and coöperation of the crushers, he has ten men on this work.

Gardner [41] reports on the examination of two samples of rubber seed oil and suggests the possibility of using this oil in industrial white paints which should resist yellowing.

Kesler, Lowy and Faragher [42] use a method based on the formation of an acid salt of rosin for purifying rosin to obtain a good yield of abietic acid. They prepared a number of new esters of abietic acid and tabulated their properties. Certain of these have commercial application as plasticizers. They developed a new method, using phosgene, for securing esters of phenols and esters with alcohols of the terpene family. The value of esters of p-toluenesulfonic acid as an esterifying reagent for preparing esters of abietic acid is shown. Van Heuckeroth [43] states that ethyl abietate, which is a pale liquid, may be used in large quantities in lacquers. It reduces the tensile strength and increases the elonga-

[38] Gardner and Levy, *Am. Paint Varnish Mfrs. Assoc. Circ.* **318:** 494 (1927).
[39] Long and Moore, *Ind. Eng. Chem.,* **19:** 901 (1927).
[40] Long, *Am. Paint Varnish Mfrs. Assoc. Circ.* **319:** 598 (1927).
[41] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **323:** 172 (1928).
[42] Kesler, Lowy and Faragher, *J. Am. Chem. Soc.,* **49:** 2898 (1927).
[43] Van Heuckeroth, *Am. Paint Varnish Mfrs. Assoc. Circ.* **318:** 489 (1927).

tion of films. Its effect on their durability is not yet known. Sward [44] reports on three samples of "recent" kauri with acid numbers from 67 to 79. In order to incorporate oil it was necessary to "run" off 30% and the resulting varnish was poor. The resins are not soluble in hydrocarbons, but are soluble in lacquer solvents, such as esters and alcohols. Such solutions are not miscible with butyl acetate nitrocotton solutions. Mory [45] discusses the use of phenol condensation products in the automotive industry and reviews the general properties and application of the resin materials and their future possibilities. Kirsopp [46] presents an outline of the types of resins that have come into the paint industry during the past 10 or 15 years and comments specifically on those synthetic resins of the phenol type that are now used in the production of quick drying oleoresin varnishes. The molecular weight of these may be as high as 1200 as compared with 500 for congo. He suggests that the high molecular weight causes films to gel more rapidly, thus producing quick drying products. These resins are hard, tough and resistant to abrasion. He refers briefly to phthalic anhydride glycerol resins, urea formaldehyde resins and cyclohexanol resins.

Rogers and Banta [47] find that cumar offers unusual possibilities as a synthetic resin. It can be used to great advantage in the formulation of lacquer when mixed with ester gum or natural resins. It gives the desirable degree of hardness to the film and produces a fine gloss and body. A lacquer formula is given in which cumar is one of the constituents.

Fisher [48] states that by heating in sheet form a mixture of rubber with about 10% of its weight of either an organic sulfonyl chloride or an organic sulfonic acid for several hours at 125-135° C., the rubber is converted into tough thermoplastic products, resembling gutta percha and hard balata. If heated similarly in bulk, there is a pronounced exothermic reaction and the products formed are hard and thermoplastic like shellac. *p*-Toluenesulfonyl chloride and *p*-toluenesulfonic acid are suitable reagents. A mixture of 7.5 parts of *p*-phenolsulfonic acid and 100 parts of rubber, under similar conditions, gives a flexible product similar to gutta percha, which is soluble in benzene and is a good adhesive. Five

[44] Sward, *Am. Paint Varnish Mfrs. Assoc. Circ.* **318**: 492 (1927).
[45] Mory, *Ind. Eng. Chem.*, **19**: 1106 (1927).
[46] Kirsopp, Abstract of Official Digest Federal Paint and Varnish Producers Clubs, Dec., 1927; *Am. Paint Varnish Mfrs. Assoc. Circ.* **320**: 9 (1928).
[47] Rogers and Banta, *Ind. Eng. Chem.*, **20**: 198 (1928).
[48] Fisher, *Ind. Eng. Chem.*, **19**: 1325 (1927).

parts of concentrated sulfuric acid, milled into 100 parts of rubber and heated as above, give balata types but not the soluble shellac type. The products have been given the general name "Thermoprene." Fisher and McColm [49] study the above reactions, chiefly the shellac-like products. After purification the chief constituent is a hydrocarbon with the same empirical formula as rubber (C_5H_8) and is 55 to 60% as unsaturated as the rubber hydrocarbon. Addition products of HCl and HBr have been prepared. Vulcanization with sulfur gives a combined sulfur content of about 21%, corresponding to 57% unsaturation as compared with rubber. Oxidation, hydrogenation, bromination, nitration, etc., have also been studied. The purified hydrocarbon is white and completely soluble in rubber solvents and insoluble in alcohol, acetone, etc. It is much more stable toward heat than rubber. The gutta percha and balata types are only partially soluble, but analysis, yields, etc., indicate that they consist of similar isomeric hydrocarbons. Gray [50] states that paint made from "thermoprene" has good adhesion to metals, resists acids, alkalies, corrosive gases and chemicals; has low permeability to moisture, salt solutions, salt spray, etc. The film is tough even at $0°$ C., and does not flake when cut; rust spreads very slowly from an exposed area. The concentration of thermoprene in the solvent can be as high as 10 to 20%. The nature of the solvent and details of making the paint are, however, not disclosed. Bradley [51] reports most remarkable adhesion and durability given to varnish films by what he calls synthetic preservative resins or "Rezyls." The nature of these resyls is, however, not disclosed but the author states they will be described by Ellis.

The American Society for Testing Materials has issued a standard specification for orange shellac,[52] a tentative method for the determination of wax in "machine made" and dry bleached refined shellac [53] and for testing shellac varnish.[54]

Kiehl [55] shows that the solvent properties of paint thinners can be determined by titrating a standard solution of kauri in butanol with the thinner. The development of sufficient cloudiness to

[49] Fisher and McColm, *Ind. Eng. Chem.*, **19**: 1328 (1927).
[50] Gray, *Ind. Eng. Chem.*, **20**: 156 (1928).
[51] Bradley, *Paint, Oil, Chem. Rev.*, **85**, no. 15: 12; no. 16: 10 (Apr. 12 and 19, 1928).
[52] Am. Soc. Testing Materials Standards, 1927, Pt. II: 241.
[53] *Proc. Am. Soc. Testing Materials*, **27**, Pt. I: 869 (1927).
[54] *Proc. Am. Soc. Testing Materials*, **27**, Pt. I: 862 (1927).
[55] Kiehl, *Am. Paint Varnish Mfrs. Assoc. Circ.* **319**: 585 (1927).

obscure printed letters is taken as the end point. Twining [56] pro-
poses a specification for mineral spirits that differs from Federal
Specifications Board Specification No. 16 and A.S.T.M. D 235-
26T by having a more restricted distillation range. The kauri-
butanol test is also mentioned but no limits are given. Gardner [57]
tests mineral spirits for sulfur by boiling with mercury and thinks
the test may be capable of better numerical evaluation than the
copper strip test. The American Society for Testing Materials
has issued a standard specification for destructively distilled wood
turpentine.[58]

Gardner [59] finds that alcohol denatured with aldehol, wood
alcohol and benzene yields shellac varnish of darker color and
lower viscosity than alcohol denatured with wood alcohol alone.
Hofmann,[60] and Reid and Hofmann [61] describe "cellosolve"
(ethyl ether of ethylene glycol), cellosolve acetate (ethylene glycol
monoethyl ether acetate) and butyl cellosolve (butyl ether of
ethylene glycol), which are finding wide application in the lacquer
industry. Davidson and Reid [62] discuss synthetic amyl acetate,
cellosolve and cellosolve acetate which, because of their higher
boiling range, are of great value as blush resisters. Gardner [63]
discusses isopropyl acetate and *sec.*-butyl acetate as nitrocellulose
solvents.

Brown and Bogin [64] discuss the proper balancing of solvents
and non-solvents in lacquers and find that empirically determined
rates of evaporation for individual solvents give more reliable
indices of evaporation tendencies than boiling point and vapor
pressure determinations. The amount of non-solvent tolerated by
a nitrocellulose solution varies with the concentration of solvent
and non-solvent. They give a number of dilution ratios for com-
mon solvents and describe the technique of making these deter-
minations by titrating a solution of nitrocellulose with non-solvent
until precipitation occurs.

Brown [65] briefly discusses the influence of the structure of
lacquer solvents on their solvent properties. Davidson and Reid [66]

[56] Twining, *Am. Paint Varnish Mfrs. Assoc. Circ.* **319**: 603 (1927).
[57] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **323**: 167 (1928).
[58] Am. Soc. Testing Materials Standards, 1927, Pt. II: 238.
[59] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **318**: 488 (1927).
[60] Hofmann, *Am. Paint J.*, **12**, no. 13: 20 (1928).
[61] Reid and Hofmann, *Ind. Eng. Chem.*, **20**: 497 (1928).
[62] Davidson and Reid, *Ind. Eng. Chem.*, **20**: 199 (1928).
[63] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **323**: 177 (1928).
[64] Brown and Bogin, *Ind. Eng. Chem.*, **19**: 968 (1927).
[65] Brown, *Ind. Eng. Chem.*, **20**: 183 (1928).
[66] Davidson and Reid, *Ind. Eng. Chem.*, **19**: 977 (1927).

conclude that (1) the dilution ratio is a reasonably accurate measure of solvent power; (2) other conditions remaining the same, the dilution ratios of nitrocellulose solvents are greater for aromatic hydrocarbons than for gasolines; (3) the glycol ethers have better dilution ratios with aromatic hydrocarbons than the butyl ethers; with gasoline the ratios are about equal; (4) cracked gasolines are better diluents than straight run gasolines of the same boiling ranges; (5) the lower boiling fractions of a given gasoline are better diluents than the higher fractions; (6) the dilution ratio decreases as the concentration of nitrocellulose is increased. Bridgman [67] investigates the evaporation rate, effect on viscosity of lacquer solutions, stability, solubility in water, depression of temperature caused by evaporation and influence on "blushing" of various high boiling solvents for nitrocellulose. Marling and Purdy [68] investigate the effect of thinners on the consistency of nitrocellulose solutions. Richardson and Sutton [69] determine the ranges of vapor concentration in air, which are explosive, for a number of lacquer solvents, describe the apparatus used, and tabulate data for single solvents and mixtures similar to those used in typical lacquers of spraying consistency. Miner [70] discusses the hazards incidental to spray painting, giving most attention to fire and explosion hazards.

Maguire [71] discusses the work of various investigators on the causes of instability of varnishes on keeping. Marling,[72] in a study of "livering" concludes that (1) the acid number of an oil has no bearing on its probable behavior with zinc oxide; (2) a knowledge of how an oil was prepared is of more value than the acid number; (3) in two oils having an acid number of 5, one containing polymerized acids as a result of kettle bodying, the other oxidized acids from blowing, the increase in body in the blown oil will be about ten times as great as with the kettle-bodied oil; (4) kettle-bodied oils when mixed with zinc oxide body more rapidly, pass the peak and begin to thin out in a shorter time than blown oils.

Gardner [73] studies methods of reducing the oil absorption of pigments and records the effects of aluminum stearate and similar

[67] Bridgman, *Ind. Eng. Chem.*, **20**: 184 (1928).
[68] Marling and Purdy, *Ind. Eng. Chem.*, **19**: 980 (1927).
[69] Richardson and Sutton, *Ind. Eng. Chem.*, **20**: 187 (1928).
[70] Miner, *Am. Paint J.*, **11**, no. 49: 7 (1927).
[71] Maguire, *Am. Paint Varnish Mfrs. Assoc. Circ.* **319**: 564 (1927).
[72] Marling, *Am. Paint Varnish Mfrs. Assoc. Circ.* **319**: 535 (1927).
[73] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **321** (1928).

metallic soaps in greatly reducing the oil required to grind a variety of pigments. Beegle and Simmons [74] and Hopkins [75] discuss the formulation, manufacture and application of lacquer surfacers. Mougey [76] discusses the different types of automobile finishes, points out the advantages of lacquer over varnish, and reviews the work of the chemist in the paint and varnish industry. Gardner [77] discusses brushing lacquers and the "four-hour" type of varnishes and enamels.

Davidson [78] describes crystal and cracked finishes and gives typical formulas. Bogin and Simms [79] determine the consistency of lacquers with an outflow pipette in comparison with glycerol. They find that a four-fold increase in consistency reduces the time available for brushing about one-half, that increase in consistency reduces the volume sprayed at a given pressure and causes a marked increase in optimum spraying pressure to produce good films, that an increase of 2% in the cotton concentration about doubles the consistency of the solution, and that it is better practice to vary consistency by changing the nitrocellulose concentration than by altering the composition of the solvent. The viscosities of solutions of various samples of 0.5 sec. nitrocellulose were found to vary over 100% and different portions of the same batch varied. Normal aging of lacquer in storage results in marked reduction in consistency and certain impurities frequently found in lacquer greatly accelerate this process. Swartz [80] describes an improved method of manufacturing cold water paint. Steele [81] studies the effect of organic bases added to the solution on the weather resistance of plasticized nitrocellulose films. Very strong bases were detrimental, many bases had no effect, others materially prolonged the life of the films. In general, the bases which had the greatest stabilizing effect caused the films to darken in color. Hofmann and Reid [82] discuss several methods of graphic representation of experimental data and their applicability to problems of the lacquer chemist, and give typical charts showing methods of calculating viscosity and specific gravity of mixtures.

Flood, Booth and Beisler [83] find that tung oil when heated in

[74] Beegle and Simmons, *Ind. Eng. Chem.*, **19**: 971 (1927).
[75] Hopkins, *Ind. Eng. Chem.*, **19**: 974 (1927).
[76] Mougey, *Ind. Eng. Chem.*, **19**: 1102 (1927).
[77] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* 322; 323: 185 (1928).
[78] Davidson, *Paint, Oil, Chem. Rev.*, **85**, no. 12: 10 (1928).
[79] Bogin and Simms, *Ind. Eng. Chem.*, **20**: 190 (1928).
[80] Swartz, *Paint, Oil, Chem. Rev.*, **85**, no. 6: 10 (1928).
[81] Steele, *Ind. Eng. Chem.*, **19**: 807 (1927).
[82] Hofmann and Reid, *Ind. Eng. Chem.*, **20**: 431 (1928).
[83] Flood, Booth and Beisler, *Ind. Eng. Chem.*, **20**: 609 (1928).

the presence of ester gum can be incorporated satisfactorily in lacquer; that it increases the durability of lacquer films and appears to make the films more adherent. Increasing amounts of dibutyl phthalate, up to the maximum used by the investigators (60% of the weight of the dry cotton), increased durability.

The Federal Specifications Board [84] has revised its specification for interior lithopone paint and Everett [85] has criticized the kauri reduction test as used in this specification. Wertz and Sanderson [86] both refuted Everett's criticism.

Bartell and Osterhof [87] describe a method for the determination of the degree of wetting of a solid by a liquid based upon the measurement of the pressure with which one liquid will displace another from a powdered material which has been compressed within a cylinder. By measuring the displacement pressure one can determine the adhesion tension between a solid and a liquid phase. Adhesion tension can be expressed in terms of absolute units, and since the adhesion tension of such a system gives a measure of the degree of wetting, the method makes possible the determination of the relative wettability of a solid by a series of liquids. Examples are given which show the relation of adhesion tension to the stability of suspensions in color varnish and lacquer systems.

Green [88] completes a series of articles on the application of the microscope to the study of pigments. He concludes that flocculation, which can be revealed by microscopic examination, is the cause of paints being plastic and is the result of interfacial tension produced when a pigment particle is immersed in a liquid vehicle. Gardner [89] describes an attachment to his mobilometer to make possible the testing of small samples. Mowen [90] describes a method for the analysis of pyroxylin lacquer and its application to the duplication of a competitor's lacquer. Ziegelmann [91] describes a method of using a centrifuge instead of a vacuum pump in determining the specific gravity of pigments.

Gardner,[92] and Gardner and Van Heuckeroth [93] describe a quantitative method of determining the adhesion and cohesion of

[84] *Bur. Standards Circ.* **111**, 3d Ed. (F.S.B. Spec. no. 21b).
[85] Everett, *Am. Paint Varnish Mfrs. Assoc. Circ.* **319**: 570 (1927).
[86] Wertz and Sanderson, *Am. Paint Varnish Mfrs. Assoc. Circ.* **319**: 578 (1927).
[87] Bartell and Osterhof, *Ind. Eng. Chem.*, **19**: 1277 (1927).
[88] Green, *Paint, Oil, Chem. Rev.*, **84**, no. 1: 16 (July 7, 1927).
[89] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **323**: 161 (1928).
[90] Mowen, *Paint, Oil, Chem. Rev.*, **85**, no. 3: 10; no. 11: 10 (1928).
[91] Ziegelmann, *Paint, Oil, Chem. Rev.*, **84**, no. 5: 12 (Aug. 4, 1927).
[92] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **323**: 155 (1928).
[93] Gardner and Van Heuckeroth, *Ind. Eng. Chem.*, **20**: 600 (1928).

films. Long, Egge and Wetterau,[93] and Gardner and Sward [94]
describe methods of making uniform varnish films. Browne dis-
cusses the causes of blistering and peeling of paint on house
siding [95] and states [96] that neither chalking nor checking can be
relied upon as indications of the protection of wood from weather-
ing by paint coatings; but that the value of coatings can be
measured by observing their effectiveness in retarding the absorp-
tion of moisture from saturated air by painted wood panels at
intervals during weather exposure. Edwards and Wray [97] agree
with Browne and call attention to the effectiveness of aluminum
paint as a priming coat. Gardner [98] has tested a number of experi-
mental coatings for metal tanks by coating polished iron and
copper bowls, and, after drying, filling the bowls to $\frac{1}{4}$ inch of the
top with 5% sodium chloride solution. The bowls were then kept
at 200° F. and the evaporated water was replaced at frequent in-
tervals. He records the condition of the bowls after 60 and 75
days. Clear coatings of oils, varnishes, resin solutions and lacquers
were unsatisfactory. Phenol aldehyde tung oil varnishes, pig-
mented with aluminum and baked, were among the best coatings
tested. Gardner and Van Heuckeroth [99] make exposure tests,
slightly accelerated by sprinkling with water each day, of a num-
ber of natural and artificial resins (1) alone, *i.e.,* cut in solvent;
(2) with solvent and oil; (3) with nitrocellulose; (4) with pig-
mented nitrocellulose. Other nitrocellulose coatings with various
plasticizers but no resins were also exposed. They give relative
ratings after 37 and 90 days and pictures illustrating types of
failure. Tensile strength and elongation tests on stripped films
indicate that good strength and fairly good elongation are charac-
teristics of fairly good resistance to weathering, while high tensile
strength and low elongation indicate lack of durability. Gregory [100]
calls attention to an accelerated test for protective coatings devised
by Dubois [101] in 1913 and states that the paints tested by Dubois
were given weather tests starting in March, 1914, and that after
11 years and 5 months the exposure tests gave results confirming
the ratings by Dubois after a few days' exposure to his accelerated

94 Gardner and Sward, *Ind. Eng. Chem.,* **19**: 972 (1927).
95 Browne, *Am. Paint Varnish Mfrs. Assoc. Circ.* **317**: 480 (1927).
96 Browne, *Ind. Eng. Chem.,* **19**: 982 (1927).
97 Edwards and Wray, *Ind. Eng. Chem.,* **19**: 975 (1927).
98 Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **323**: 133 (1928).
99 Gardner and Van Heuckeroth, *Am. Paint Varnish Mfrs. Assoc. Circ.* **316** (1927).
100 Gregory, *Ind. Eng. Chem.,* **19**: 1225 (1927).
101 Dubois, *Ind. Eng. Chem.,* **5**: 968 (1913).

test. Jenkins and Croll [102] describe their methods of testing finished lacquers, including equipment for accelerated weathering tests similar to the well-known Nelson equipment using quartz mercury arc light, water and refrigeration. Lacquer films are tested for elongation and tensile strength with a Mullen paper tester with a simple attachment for indicating the elongation. A paper curling test is recommended as useful in indicating lack of sufficient plasticizer. Two methods for determining sanding properties of the films are given. Gardner [103] describes an accelerated exposure equipment. The test panels are placed in a cylinder having an equal-arm rotating cross at the center. Two opposite arms have at their ends inclosed carbon arc lights and the ends of the other arms carry water sprays. Sudden cooling is accomplished by clamping metal refrigerating cans to the back of the metal panels and pouring a mixture of solid CO_2 and acetone into the cans. Photographs show the type of failure produced in a number of coatings. Walker and Hickson [104] describe the equipment used at the Bureau of Standards for accelerated testing of organic protective coatings. The cycle of exposure includes light from an inclosed carbon arc, water, ozonized air and refrigeration. A variety of materials, including varnishes, oil paints, enamel paints, lacquers, bituminous saturated felts, and bituminous roofing materials, that have been tested in the proposed accelerated cycle, show, as judged by visual inspection, the same nature of breakdown as that observed on outdoor exposure. The authors point out the large errors in ratings by visual inspection and the necessity of developing methods for the quantitative measurement of rate of deterioration. Several methods designed for this purpose are described. These include measuring the amount of water vapor under definite conditions or amount of air under definite pressures passing through coatings on wire gauze, and several plans for locating and measuring breaks in a coating on metal by electrical means.

[102] Jenkins and Croll, *Ind. Eng. Chem.*, **19**: 1356 (1927).
[103] Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.* **323**: 141 (1928).
[104] Walker and Hickson, *Ind. Eng. Chem.*, **20**: 591 (1928).

Chapter XLV.

Leather.

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American leather chemists have made very considerable progress during the current year in adding to our knowledge of the science of tanning.

Raw Skin. Imes [1] has made a preliminary report upon the investigation of the Bureau of Animal Industry as to the occurrence, extent and control of the cattle skin disease termed "follicular mange" (demodectic scabies) in the United States.

Soaking. Theis [2] has determined some of the constants of skin fats and certain of the changes which they undergo in soaking and liming. Theis and McMillen [3] have studied certain changes which the skin proteins undergo in soaking, finding the basic nitrogen to decrease and a corresponding increase in the non-basic, as a function of time of soak.

Unhairing. McLaughlin and O'Flaherty [4] have studied the histologic changes which skin undergoes in the unhairing process, in the presence of lime only, lime plus sodium sulfide and lime plus amines. McLaughlin, Rockwell and Blank [5] have investigated the bacteriology of the liming of skin, finding that bacteria are not active in any normal tannery lime liquor but that the bacterial history of the skin prior to liming largely determines its chemical behavior in the lime solution. McLaughlin, Highberger and Moore [6] have demonstrated that the action of lime solutions upon skin is purely chemical in nature and have shown that at the point of hair slippage (regardless of time required for slip-

[1] Imes, *J. Am. Leather Chem. Assoc.,* **22**: 531 (1927).
[2] Theis, *J. Am. Leather Chem. Assoc.,* **23**: 4 (1928).
[3] Theis and McMillen, *J. Am. Leather Chem. Assoc.,* **23**: 226 (1928).
[4] McLaughlin and O'Flaherty, *J. Am. Leather Chem. Assoc.,* **22**: 323 (1927).
[5] McLaughlin, Rockwell and Blank, *J. Am. Leather Chem. Assoc.,* **22**: 329 (1927).
[6] McLaughlin, Highberger and Moore, *J. Am. Leather Chem. Assoc.,* **22**: 345 (1927).

page) a definite minimum amount of sulfur is found dissolved in the lime solution. This dissolved sulfur is derived mainly from the keratin of the skin epidermis, which holds the hair in the follicle. They show, also, that the heightened unhairing power of a re-used lime solution is not due—as has been variously held—to the presence of accumulated bacteria, enzymes, ammonia or sulfur, but to the presence of small quantities of primary amines, formed largely through the action of proteolytic bacteria upon the skin during the processes preceding liming.

Merrill and Fleming [7] studied the hydrolysis of skin and hair by saturated lime solution, as a function of temperature. At temperatures below 35° C. hair is hydrolyzed more rapidly than skin; the reverse occurs at higher temperatures. They feel these results support the theory that collagen hydrolysis consists mainly of the opening up of secondary valence bonds. Hydrolysis of keratin involves the breaking of a primary valence bond, probably the —S—S— linkage of cystine.

Chrome Tanning. Gustavson [8] has pointed out, as a result of his work, that the degree of chrome fixation by skin is not regulated by the hydrogen-ion concentration of the chrome solution but is largely governed by the composition of the chrome salt. As pointed out by last year's reviewer, it is impossible to adequately present the valuable researches of Gustavson on chrome tanning in the small space here available.

Other Methods of Tanning. Li [9] studied the tanning properties of a large number of naphthalene derivatives and other organic compounds and advanced the theory that their combination with skin proteins is chemical in nature; the combination occurring between the skin NH_2 groups and the OH groups of the tanning agents. The position of the OH groups must be near the center of the molecule (as in α-naphthol). Two OH groups must occupy symmetrical positions near the extremities of the molecule. Thus the required "balanced" molecular structure is obtained.

Niedercorn [10] studied the tanning of calf skin by the sulfates of tervalent molybdenum, the purple-red and the green. The former tanned at pH 1.0 to 1.5, the latter at 2.0 to 2.5. Both produced a brown leather which withstood the action of boiling water,

[7] Merrill and Fleming, *Ind. Eng. Chem.*, **20**: 21 (1928).
[8] Gustavson, *Ind. Eng. Chem.*, **19**: 1015 (1927).
[9] Li, *J. Am. Leather Chem. Assoc.*, **22**: 380 (1927).
[10] Niedercorn, *Ind. Eng. Chem.*, **20**: 257 (1928).

but, upon standing in air, this property was lost, both leathers shrinking and hardening.

Thomas and Kelly [11] investigated the fixation of aluminum and of iron by hide substance, with particular reference to the reversibility of the compounds (leather) formed. The aluminum fixed by hide substance, when normal aluminum chloride or sulfate are employed, may be almost completely removed by washing the leather with water. If the pH value of the aluminum solutions is increased (*i.e.*, if they are rendered more basic) an irreversible fixation or tanning occurs and increases with rise of pH. Irreversible fixation with iron, however, takes place in the case of normal ferric sulfate, although increase of basicity heightens fixation. The presence of sodium chloride or sulfate retards aluminum fixation. Sodium chloride diminishes iron fixation, whereas the sulfate may—under certain conditions—favor it.

Plumping. Page and Page [12] found that the effect of the presence of neutral salts upon the acid or alkali plumping of skin varied with the pH value of the solution, the concentration of the salt employed and its character.

Fat Liquoring. Wilson [13] has studied the quantity of egg constituents required to stabilize a watery emulsion of leather oils, and the proper treatment of leather with such emulsions.

Buncke [14] has investigated the suitability of sulfonated oils for leather, as a function of their composition and their degree of sulfonation.

Merrill [15] found that the penetration of oil into leather in fat liquoring increases with pH value and is only slightly affected by increasing concentration of oil, ratio of oil to leather or time of fat liquoring, whereas the *total* oil taken up (ignoring its penetration depth) is but little affected by pH value, but is markedly changed by the other factors enumerated.

Merrill [16] showed that, if chrome upper leather is fat liquored with an emulsion of pure sulfonated oil, the leather will contain approximately the same quantity of oil—per unit volume of skin —in both its grain (hair side) and flesh (adipose side) layers. But, owing to the lesser density of the grain layer, this portion will contain more oil per unit *weight* of skin. The addition of egg

[11] Thomas and Kelly, *Ind. Eng. Chem.*, **20**: 628, 632 (1928).
[12] Page and Page, *Ind. Eng. Chem.*, **19**: 1264 (1927).
[13] Wilson, *J. Am. Leather Chem. Assoc.*, **22**: 559 (1927).
[14] Buncke, *J. Am. Leather Chem. Assoc.*, **22**: 621 (1927).
[15] Merrill, *Ind. Eng. Chem.*, **20**: 181 (1928).
[16] Merrill, *Ind. Eng. Chem.*, **20**: 654 (1928).

to the emulsion, however, results in more oil being taken up by the flesh and less by the grain. Merrill offered a tentative explanation of this phenomenon by suggesting that the addition of egg so increases the size of the emulsion droplets that they have difficulty in penetrating the smaller openings of the grain but can enter the larger openings of the flesh.

Enzymes. Merrill and Fleming [17] showed that trypsin digests the collagen of limed and unlimed calf skin at the same rate. The unlimed skin contains a greater amount of material easily digested by trypsin; this material consists, probably, of degradation products of the proteins of the fresh skin.

Leather Book Binding. Veitch, Frey and Leinbach [18] analyzed the bindings of some very old books, the bindings being in excellent condition, and conclude their durability to result from the low acid content of the leather (none showing more than 0.53%, presumably sulfuric) and the fact that they seem to have been tanned with pyrogallol tannins.

Analytical Methods. Numerous reports upon analytical methods have been published. Balderston [19] reported on the determination of nitrogen in leather, Veitch and Jarrell [20] on the determination of water in leather, Mlejnek [21] on the separation of catechol and pyrogallol tannins, Porter [22] on the plumping of skin in tan liquors, Reed [23] on tannin analysis, Bowker and Wallace [24] on the effects of acid in leather, Orthmann [25] on the determination of dry skin substance in hides and skins, Clarke and Frey [26] on the determination of sugars in tanning materials, Orthmann [27] on a method for determining rate of water absorption by leather, and Merrill, Niedercorn and Quarck [28] on the differentiation of the sulfate bound by protein in chrome leather and that held by the chromium salt.

The first of the two volumes of the second edition of J. A. Wi'son's "Chemistry of Leather Manufacture" has been printed. This text has been very excellently done and constitutes a valuable addition to the literature.

[17] Merrill and Fleming, *J. Am. Leather Chem. Assoc.*, **22**: 275 (1927).
[18] Veitch, Frey and Leinbach, *J. Am. Leather Chem. Assoc.*, **23**: 9 (1928).
[19] Balderston, *J. Am. Leather Chem. Assoc.*, **22**: 261 (1927).
[20] Veitch and Jarrell, *J. Am. Leather Chem. Assoc.*, **22**: 265 (1927).
[21] Mlejnek, *J. Am. Leather Chem. Assoc.*, **22**: 470 (1927).
[22] Porter, *J. Am. Leather Chem. Assoc.*, **22**: 521 (1927).
[23] Reed, *J. Am. Leather Chem. Assoc.*, **22**: 635 (1927).
[24] Bowker and Wallace, *J. Am. Leather Chem. Assoc.*, **23**: 82 (1928).
[25] Orthmann, *J. Am. Leather Chem. Assoc.*, **23**: 1 (1928).
[26] Clarke and Frey, *J. Am. Leather Chem. Assoc.*, **23**: 91 (1928).
[27] Orthmann, *J. Am. Leather Chem. Assoc.*, **23**: 184 (1928).
[28] Merrill, Niedercorn and Quarck, *J. Am. Leather Chem. Assoc.*, **23**: 187 (1928).

Chapter XLVI.

Rubber.

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General. A parliamentary decision of prime importance to the rubber industry is the announcement of the abrogation of the Stevenson Restriction Act, November 1, 1928. The "natural" law of supply and demand will then once more be in effect in all the countries growing crude rubber.[1]

The Rubber Division of the American Chemical Society has been enlarging its influence and extending its activities by publishing a new journal, "Rubber Chemistry and Technology," and by holding group meetings in the larger centers such as Boston, New York, Akron and Los Angeles. The new journal under the editorship of C. C. Davis began its quarterly appearance in April, 1928. For the present it will contain chiefly reprints of the important rubber articles published in the United States and abroad, translations, reports, etc. Its publication is being made possible largely through the financial aid of the Rubber Association of America, which is also financing the work of the Physical Testing Committee of the Rubber Division.

An outline of the contributions of rubber chemistry to the automotive industry has been given by Geer.[2]

The Ford rubber concession in the Amazon Valley is the beginning of an important development.[3]

A new method of improving the quality of guayule rubber has been announced by Spence.[4] It was developed in part on the discovery by McCallum that the rubber exists in the plant juices of the roots, stems and branches of the guayule shrub in the form

[1] Perry, *India Rubber World*, **78**: 53 (1928).
[2] Geer, *Ind. Eng. Chem.*, **19**: 1095 (1927).
[3] *India Rubber World*, **77**: 56 (1927).
[4] Spence, *Rubber Age* (N.Y.), **23**: 133 (May 10, 1928); Sauchelli, *India Rubber World*, **78**, no. 3: 55 (1928).

of a colloidal suspension instead of as formerly believed in the form of solid rubber. The new method consists of a retting process prior to the mechanical extraction of the rubber. The chief results are the reduction of the resin content from 20-25% to about 10% and a noteworthy improvement in the properties of the vulcanized product.[5]

Park, Carson and Sebrell [5a] have made a comprehensive study of the effect of heat on various types of raw rubber at vulcanizing temperatures. Heating in steam for 24 hours at 158° C. increases the plasticity, the acetone extract, the acid number and, in some cases, the rate of vulcanization, and decreases the total nitrogen. Hydrolysis of proteins and esters and loss of volatile compounds explains some of these changes. The stress-strain curve of the vulcanizates becomes more convex toward the strain axis, and the aging is not impaired. The authors believe that the simple nitrogen bases and alkaloids are the principal active materials responsible for the peculiarities of heated rubber.

Latex. Studies on latex in this country have appeared infrequently, chiefly in the patent literature. Two important foreign articles on preserved latex and cream from latex have been published by de Vries and Beumée-Nieuwland,[6] and the first description of the commercial operation of the "Revertex" process has been described by Hauser and Fould.[7] "Revertex" is the name of a heavy paste containing about 75 parts of rubber which is obtained by the concentration of latex in the presence of alkali and a stabilizer.

Chemical Reactions of the Rubber Hydrocarbon. Kemp [8] has shown that, by heating rubber mixed with 8 to 16% of sulfur to temperatures of 200-280° C., it is converted into a material with the thermoplastic properties of gutta-percha. These temperatures are much higher than the ordinary vulcanizing temperatures, 110-150° C.

Bruson, Sebrell and Calvert [9] have shown that the rubber hydrocarbon adds the halide salts of tin, iron, antimony and titanium, forming colored addition compounds. They isolated and studied the stable addition product with stannic chloride which was found

[5] Spence and Boone, Bur. Standards, *Tech. Paper,* no. **353** (1927); *India Rubber World,* 77: 65 (1928).
[5a] Park, Carson and Sebrell, *Ind. Eng. Chem.,* **20**: 478 (1928).
[6] deVries and Beumée-Nieuwland, *Arch. Rubbercultuur,* **11**: 289, 371 (1927).
[7] Hauser and Fould, *India Rubber J.,* **74**: 700 (1927).
[8] Kemp, U.S.P. 1638535 (Aug. 9, 1927).
[9] Bruson, Sebrell and Calvert, *Ind. Eng. Chem.,* **19**: 1033 (1927).

to have the empirical formula $(C_5H_8)_{10} \cdot SnCl_4$. Treatment of this compound with alcohol eliminates the stannic chloride and at the same time precipitates a white, amorphous solid having the same formula as rubber $(C_5H_8)_x$, and being less unsaturated than rubber. It could be separated into two substances, one soluble and one insoluble in benzene. The authors believe that the formation of these two substances substantiates the theory of the existence of a two-phase system in the original rubber.

Fisher [10] has developed methods of preparing in large quantities conversion products of rubber which are thermoplastic and resemble gutta-percha, balata and shellac. They are prepared by heating under various conditions mixtures of rubber with approximately 10% of its weight of an organic sulfonyl chloride or an organic sulfonic acid. Five per cent of concentrated sulfuric acid also produces somewhat similar products. The purified products have been shown by Fisher and McColm [11] to be hydrocarbons of the same composition as that of rubber, $(C_5H_8)_x$. These "thermoprenes," as they are called, are, however, generally 55 to 60% as unsaturated as rubber and are therefore polycyclic forms of rubber. Vulcanization transforms them into insoluble products like hard rubber. Several chemical addition products have been prepared from them.

Gray [12] has described the use of some of the thermoprenes as protective paints.

Other methods of converting rubber into thermoplastic products having the same chemical composition but less unsaturation than rubber have also been described by Fisher. [13] They consist of heating rubber in solution with or without a phenol at steam-bath temperatures. A mixture of 100 parts of rubber, 20 of resorcinol and 20 of trichloroacetic acid, heated in a vulcanizing press for 20 hours at 162° C., is converted into a hard, very tough, practically insoluble product resembling hard rubber.

Kemp, Bishop and Lackner [14] have continued Kemp's [15] application of the Wijs iodine-chloride method to the determination of the rubber hydrocarbon and have applied it to the analysis of vulcanized rubber goods. They have also verified previous work, finding that the total rubber hydrocarbon can be calculated from

[10] Fisher, *Ind. Eng. Chem.*, **19**: 1325 (1927).
[11] Fisher and McColm, *Ind. Eng. Chem.*, **19**: 1328 (1927).
[12] Gray, *Ind. Eng. Chem.*, **20**: 156 (1928).
[13] Fisher, U.S.P. 1642018 (Sept. 13, 1927).
[14] Kemp, Bishop and Lackner, *Ind. Eng. Chem.*, **20**: 427 (1928).
[15] Kemp, *Ind. Eng. Chem.*, **19**: 531 (1927).

the value determined by the iodine-chloride method plus the value calculated from the amount of combined sulfur, assuming that each atomic equivalent of sulfur saturates the double bond in a C_5H_8 group.

The unsaturation of rubber vulcanized with polynitro compounds and with benzoyl peroxide has been determined by Fisher and Gray.[16] Using the Kemp-Wijs method, they found that, within the experimental error of 0.5%, the unsaturation in each case was the same as before vulcanization. If any oxygen is added it must be very low in amount—less than 0.14% as calculated from the probable error in the method.

In this section it should also be mentioned that Macallum and Whitby[17] have prepared a new tetramethyl-butadiene, 3,4-dimethylhexa-2,4-diene. It did not undergo thermopolymerization when heated at 100° C. at 28 mm. pressure, nor was it polymerized by long standing with sodium. These facts with others cited in the article show that not all butadiene derivatives polymerize under the same conditions as butadiene itself and isoprene. This is an interesting commentary on some of the substances blindly covered in patents on synthetic rubber. Macallum and Whitby[18] have also described several derivatives of 2,3-dimethyl-1,3-butadiene, prepared from its dibromide. Bruson and Calvert[19] have found that one molecular equivalent of thiocyanogen adds to isoprene, forming the solid compound $C_5H_8(SCN)_2$, and that 2,3-dimethyl-1,3-butadiene reacts similarly.

Accelerators. The patent announcements continue to contain the names of new accelerators but those given during the last year are derivatives of known types.

Hardman and White[20] have published some interesting information on the amount of sulfur combined during vulcanization in the presence of various types of accelerators. It is well known that the amount varies and does not correlate at all with the physical properties of the vulcanizate. When the accelerator is decomposed during vulcanization the rate of combination of sulfur decreases with the time and with accelerators which are stable during vulcanization the rate is similar to that when no accelerator is used. The first or transient type is exemplified by zinc ethyl-

[16] Fisher and Gray, *Ind. Eng. Chem.*, **20**: 294 (1928).
[17] Macallum and Whitby, *Trans. Roy. Soc. Can.*, **22**: 39 (1928).
[18] Macallum and Whitby, *Trans. Roy. Soc. Can.*, **22**: 33 (1928).
[19] Bruson and Calvert, *J. Am. Chem. Soc.*, **50**: 1735 (1928).
[20] Hardman and White, *Ind. Eng. Chem.*, **19**: 1037 (1927).

xanthate and lead dithiofuroate and the second or stable type by hexamethylenetetramine and triphenylguanidine. The majority of important accelerators lie between these two extremes and consist of diphenylguanidine, tetramethylthiuram monosulfide, zinc dithiocarbamate, etc.

The activity of certain aryl-substituted biguanides has been reported on by Smith and Weiss.[21] They found that a,a-diphenylbiguanide was the most active of those studied. Like the diarylguanidines they are relatively inactive in the absence of zinc oxide.

Of considerable commercial and patent importance is the announcement of the Supreme Court of the United States that the Weiss diphenylguanidine patent is invalid.[22]

Aging. An excellent and important piece of work has been carried out by Bruson, Sebrell and Vogt,[23] who have isolated from the unsaponifiable matter of the acetone extract two natural oxidation inhibitors of crude Hevea rubber. They appear to be liquid sterols having the composition $C_{27}H_{42}O_3$ and $C_{20}H_{30}O$, and occur in pale crepe to the extent of about 0.08 and 0.16%, respectively. When acetylated and hydrogenated they lost their antioxidant power. A third phenolic antioxidant possessing strong reducing action occurs in the aqueous extract. The stability of crude rubber in air is dependent upon the presence of these naturally occurring antioxidants which, when removed by acetone extraction, leave the rubber in a state that is readily susceptible to autoxidation and to formation of tacky products.

Tener, Smith and Holt,[24] at the Bureau of Standards, have studied the influence of light, heat, oxygen, moisture, composition and degree of vulcanization on the rate of deterioration of soft rubber goods. The work is extensive and confirms many other observations.

A paper by Kelly, Taylor and Jones [25] records that the stretching of vulcanized rubber in sunlight, ultra violet light and the 70° C. aging oven, accelerated the rate of deterioration but the rate of deterioration was not proportional to the degree of stretching. During the early stages in sunlight there was a critical elongation at which deterioration was more rapid in each case but later

[21] Smith and Weiss, *Ind. Eng. Chem.*, **20**: 298 (1928).
[22] *Rubber Age* (N.Y.), **23**: 79 (1928).
[23] Bruson, Sebrell and Vogt, *Ind. Eng. Chem.*, **19**: 1187 (1927).
[24] Tener, Smith and Holt, Bur. of Standards, *Tech. Paper no.* **342**: 353 (1927).
[25] Kelly, Taylor and Jones, *Ind. Eng. Chem.*, **20**: 296 (1928).

the greater the elongation the faster the deterioration. Somewhat similar results were obtained by Haushalter, Jones and Schade [26] when samples of stretched rubber were exposed to air containing ozone. The conditions were more severe because samples elon- gated only 0.1% cracked in a few minutes. In the unstretched state they were far less sensitive to ozone. It is a surface phe- nomenon and physical tests did not indicate a decline in quality.

Judged by the oxygen bomb test, 0.1% cupric stearate, 0.1% manganic oleate, 0.5% ferric stearate or surface treatment with cupric chloride, hastens deterioration of a tread compound whereas 1% of mercuric stearate does no harm, according to Taylor and Jones.[27]

McKee and Depew [27a] have recorded the "normal" aging of nine widely different types of cured rubber mixtures over a period of four years, under varying conditions of light, humidity and temperature, and under strain in some cases. The extensive data obtained are given in numerous curves. Paraffin and zinc oxide retarded the action of light and there is probably a close relation between the protection of paint and of rubber from deterioration by light.

After aging rubber bands from different sources for $3\frac{1}{2}$ years under various conditions, Boone [28] concludes that the Geer 70° C. air oven aging test gives a good general indication of the relative aging properties of such goods.

Compounding Ingredients or Pigments. The physical and chemical characteristics of several carbon blacks and of rubber stocks containing them have been investigated by Goodwin and Park [29] in order to determine their suitability as pigments in tire- tread stocks. The first part is very complete and represents a study of the properties of the blacks themselves and their use in raw rubber. Johnson [30] has given data on the absorption and re- moval of moisture from stored carbon black, and has devised an instrument [31] for distinguishing the color of carbon blacks by measuring comparatively the quantity of light reflected.

An interesting theoretical discussion is given by Greene [32] on the effect of non-uniformity and particle shape on the meaning of

[26] Haushalter, Jones and Schade, *Ind. Eng. Chem.*, **20**: 300 (1928).
[27] Taylor and Jones, *Ind. Eng. Chem.*, **20**: 132 (1928).
[27a] McKee and Depew, *Ind. Eng. Chem.*, **20**: 484 (1928).
[28] Boone *India Rubber World*, **76**: 317 (Sept., 1927).
[29] Goodwin and Park, *Ind. Eng. Chem.*, **20**: 621 (1928).
[30] Johnson, *Rubber Age* (N. Y.) **22**: 535 (1928).
[31] Johnson, *India Rubber World*, **77**: 65 (Feb., 1927).
[32] Green, *J. Franklin Inst.*, **204**: 713 (1927).

"average particle size." Much has been written on the average particle size but so far little explanation has been offered. He states that there is no general average particle size, the particle size must be given as some definite average diameter which will depend upon the use to which it is to be put and that the non-uniformity introduces complexity but no insurmountable difficulties so long as the mass of particles possesses geometrical similarity. The use of the formulas of the average diameter obtained on the basis of geometrical similarity is adopted for all cases of geometrical dissimilarity. It is shown that this step not only simplifies matters but is permissible when arbitrary values are not assigned to the shape factors.

Physical Properties and Methods of Testing. In a valuable scientific paper from the Bureau of Standards [33] important data are given by McPherson, and by Curtis, McPherson and Scott on the density and the electrical properties of the system: rubber-sulfur. These properties were measured for the range of composition from 0 to 32% of sulfur,—from crude rubber to hard rubber. The density is greater after vulcanization than before, the difference increasing to a maximum of about 0.060. The relation between density and composition may be represented approximately by a linear curve with a discontinuity in slope at 19% of sulfur, the composition of which corresponds to $(C_5H_8)_2S$. The volume change increases with increasing proportion of sulfur up to 19%, thence forward it is approximately constant. The coefficient of thermal expansion of rubber-sulfur mixtures decreases with increase in the per cent of combined sulfur, but the relation is not linear and at 19% of sulfur a tremendous decrease takes place, the rate of decrease then becoming slower again. The electrical properties also depend upon the amount of combined sulfur. A study of the values for the dielectric constant, the power factor, and the resistivity, and the density indicates the existence of a definite compound of the empirical formula $(C_5H_8)_2S$, and with less certain indications of the compounds $(C_5H_4)_4S$, $(C_5H_8)_3S$ and $(C_5H_8)_4S_3$. It is impossible to tell the full meaning of these facts until further work is done.

In another report from the Bureau of Standards, Tener, Kingsbury and Holt [34] record the tensile strength and elongation of several soft rubber compounds at temperatures ranging from — 70 to

[33] McPherson. Bur. Standards, *Sci. Paper* no. **560**: 385 (1927).
[34] Tener, Kingsbury and Holt, Bur. Standards, *Tech. Paper* no. **364**: 367 (1928).

$+ 147°$ C. All the stocks lost their elasticity at about $- 60°$ C. The curves shown are very illuminating and should be of considerable use in the design of rubber articles which are to be used at other than ordinary temperatures.

The influence of the sulfur-rubber ratio on the physical properties of hard rubber is discussed by Pearsall.[35] When the ratio is below 0.30 the physical strength is poor and the flexibility and flow under stress or when heated is too great. The strength was practically a maximum and the deflection a minimum at a ratio of 0.45. Mixtures with ratios between these values are the most desirable for general use.

Vogt [36] has devised an angle abrasion machine and given comparative data with others, and has discussed the analysis of such a machine.

An instrument for determining the brittleness of rubber and gutta-percha compounds has been developed by Kohman and Peek.[37] It measures the highest temperature at which a material will fracture under standardized conditions. Some of the results are $- 58°$ C. for pale crepe; $- 57°$ C., smoked sheet; $- 55°$ C., purified rubber hydrocarbon; $- 53°$ C., vulcanized rubber; $- 28°$ C., gutta-percha; and $- 44°$ C. for balata.

Zimmerman and Brown [38] have made a hardness tester for rubber; it is of the penetrometer type. The rubber is under a predetermined definite pressure and the instrument is aligned with the surface which is compressed.

Warner,[39] describing seven years' experience with a mill room testing laboratory which took care of the cure, hardness, stretch, specific gravity, color, and plasticity of stocks, stated that the methods used practically eliminated the common factory troubles which are ordinarily accredited to the compounder.

An 81-page pamphlet issued by the Bureau of Standards [Circular No. 38 (1927)] contains considerable information of general interest, and methods of testing.

The importance of temperature and humidity control in rubber testing is taken up by the progress report of the Physical Testing Committee of the Rubber Division of the American Chemical Society.[40] The normal daily variation of temperature may influence

[35] Pearsall, *India Rubber World, 77:* 70 (Dec., 1927).
[36] Vogt, *Ind. Eng. Chem.,* 20: 302 (1928).
[37] Kohman and Peek, *Ind. Eng. Chem.,* 20: 81 (1928).
[38] Zimmerman and Brown, *Ind. Eng. Chem.,* 20: 216 (1928).
[39] Warner, *India Rubber World, 77:* 5 (Oct., 1927).
[40] *Rubber Age* (N.Y.), 22: 245 (1927); *Rubber Chem. Tech.,* 1: 182 (1928).

the physical tests as much as does a 25-40% change in the time of vulcanization. With change in relative humidity the physical tests change comparatively little. Variations in the absolute humidity before curing may influence the tensile strength and modulus as much as do variations in the temperature after curing.

The influence of temperature on the tensile strength of reclaimed rubber is shown by Palmer [41] to cause losses of from 16 to 24% between 20 and 30° C.

The manufacture and testing of rubber-coated automobile fabrics is described by Nickowitz.[42]

Reclaimed Rubber. Considerable activity in this field is apparent and some very useful papers were brought out by the symposium on reclaimed rubber held by the Rubber Division at its Detroit Meeting.

Cartlidge and Snyder [43] found that the best quality and longest optimum range of cure were obtained when 2 to 2.5% of sulfur, based on the whole reclaim, was used in conjunction with 4% of sulfur for the new rubber.

Winkelmann and Croakman [44] have shown that when large proportions of carbon black, whiting, barytes, blanc fixe and mineral rubber are used with reclaimed rubber, only carbon black has a marked reënforcing effect. Cranor [45] independently reached the same conclusions.

Attempts to find out why stocks containing reclaimed rubber vulcanize more rapidly than those with crude rubber alone have been made by Shepard, Palmer and Miller.[46] Traces of alkali remaining from the reclaiming process may account for part of the difference. Pale crepe when heated in water under reclaiming conditions vulcanized the same as when unheated.

Shoaff [47] has given an excellent discussion of the factors involved in reclaiming rubber.

Vogt [48] emphasizes the fact that any method of compounding which involves direct substitution of reclaimed rubber hydrocarbon for new rubber hydrocarbon without further compensation and adjustment of other ingredients will give inferior quality.

[41] Palmer, *Ind. Eng. Chem.*, **19**: 1030 (1927).
[42] Nickowitz, *Rubber Age* (N.Y.), **22**: 77 (1927).
[43] Cartlidge and Snyder, *Ind. Eng. Chem.*, **20**: 137 (1928).
[44] Winkelmann and Croakman, *Ind. Eng. Chem.*, **20**: 134 (1928).
[45] Cranor, *India Rubber Tire Rev.*, **27**: nos. 10, 20, 22, 26, 36 (1927).
[46] Shepard, Palmer and Miller, *Ind. Eng. Chem.*, **20**: 143 (1928).
[47] Shoaff, *Ind. Eng. Chem.*, **20**: 152 (1928).
[48] Vogt, *Ind. Eng. Chem.*, **20**: 140 (1928).

Conclusion. Important advances have been made in the chemical and physical properties of rubber and in the scientific use of reclaim. Work has been in progress in this country on the synthesis of rubber but no publications have come forth. Will the drop in the price of crude rubber make any changes in this most interesting and important work?

Mention should also be made of some of the important theoretical work in addition to that already given that is being done by our scientific co-workers in Europe: Pummerer [49] has continued his work on the purification of the rubber hydrocarbon, its molecular weight, etc.; the work of Katz,[50] and Hauser [51] on their X-ray investigations of the constitution of rubber deserves careful study; derivatives of rubber through the action of nitroso compounds by Bruni and Geiger [52] and others through the phenol condensation products of rubber bromide by Geiger; [53] Bishop's [54] work on the proteins in latex; and Stevens' [55] recent article on the nature of vulcanization.

[49] Pummerer, Nielsen and Gundel, *Ber.*, **60**: 2163 (1927); Scheibe and Pummerer, *Ber.*, **60**: 2167 (1927); *Rubber Chem. Tech.*, **1**: 163, 167 (1928).
[50] Katz, Selmann and Heyne, *Kautschuk*, **1927**: 215; Katz, *Gummi-Ztg.*, **41**: 2035, 2091 (1927); *Chem.-Ztg.*, **51**: 381 (1927).
[51] Hauser, *Kautschuk*, **1927**: 228.
[52] Bruni and Geiger, *Rubber Chem. Tech.*, **1**: 177 (1928).
[53] Geiger, *Helvetica Chim. Acta*, **10**: 530 (1927).
[54] Bishop, *Malayan Agr. J.*, **15**: 271 (1927).
[55] Stevens, *J. Soc. Chem. Ind.*, **47**: 37T (1928).

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